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THE INSTITUTE OF PETROLEUM.

AN Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, November 10, 1948, the President, Mr E. A. Evans, occupying the Chair.

The Minutes of the preceding Ordinary Meeting, held on October 14, 1948, were read, confirmed, and signed.

MR GEORGE SELL (Editor) announced the names of those who had been elected to membership of the Institute in accordance with the By-Laws.

THE PRESIDENT: It is with very considerable satisfaction that we have listened to the list of Member-Companies which has been read. The response from the industry is satisfactory, and we look forward to more companies joining us. We have not yet approached the biggest companies, because first we want to see what the response will be from what we might call the lesser brethren.

THE PRESIDENT: This evening we are to have the privilege of listening to a paper by Mr A. R. W. Baddeley, Dr A. H. Nissan, and Professor F. H. Garner.

It is perfectly clear that the paper is the result of work which has been conducted in the University of Birmingham. We have become so accustomed to a high standard of quality that we are rather inclined to shudder for Mr Baddeley who has undertaken the responsibility of upholding that very great tradition in presenting the paper; but I am sure he has been sufficiently well trained in the art and the science and perhaps the rhetoric that we shall have a very enjoyable presentation.

MR BADDELEY then presented the following paper:

DETERGENCY OF CARBON BLACK IN HYDROCARBON SOLUTION. PART I.

By A. R. W. BADDELEY (Student Member), A. H. NISSAN (Fellow), and F. H. GARNER (Fellow).

SUMMARY.

The ability to retain carbon in suspensions of lubricating oil is commonly described as detergency, although the problem is one of both cleansing and dispersion. Suspensions of carbon black (Micronex) in toluene solutions of calcium naphthenate were studied in order to determine the degree of dispersion and the adsorption of calcium naphthenate on the carbon black.

The degree of dispersion was determined by measuring the rates of settling of the suspensions over a period of time of 48 hr, and it was found that with increasing concentrations of calcium naphthenate a more uniform rate of settling was obtained, showing that better dispersion of the carbon black had been obtained. The adsorption of calcium naphthenate on the carbon black

was determined by measuring the concentration of calcium naphthenate in the clear solution from which the carbon black had settled out; force-area curves obtained on the Langmuir trough were used to determine the concentration.

The degree of dispersion as measured above and the adsorption of calcium naphthenate on the carbon black approached a maximum at about 0·188 per cent calcium-naphthenate concentration in toluene. Thus in this single series of experiments the minimum concentration of calcium naphthenate to give maximum degree of dispersion can be determined from the adsorption isotherm for calcium naphthenate on carbon black on a series of concentrations. It is of interest to note that with the series of suspensions of Micronex (carbon black) ranging from 0·1 to 1 g in 25 ml of solution, the maximum adsorption was reached in all cases at about the same figure, namely 0·094 to 0·188 per cent concentration of calcium naphthenate in toluene.

Introduction.

The term "detergency," as applied to lubricating oils, describes the property of maintaining finely divided matter and particularly so-called "carbon" in the lubricating oil in suspension: such carbon tends to deposit in the crankcase and in oilways and may interfere with the supply of lubricating oil to bearings. The word "detergency," however, implies a cleansing action—literally wiping off—and the removal of carbon from metallic surfaces is a property of detergent oils. As the characteristic feature of "detergent oils" is that of maintaining the carbon dispersed throughout the oil, probably "dispersivity" would be a more accurate term to describe this action. Nevertheless, the term "detergent oils" will be used here in the general sense of maintaining dispersion of particles in oils.

Detergency is normally applied to the action of soap and the newer synthetic materials in cleansing, but these act in the presence of water. The detergent molecules are usually of the anion-active or cation-active type, and it is these active radicles which are responsible for the surface activity, micelle formation, and colloidal behaviour,[1] involving wetting of the solid surface and removal of loosened soil from the surface in such a form that it is not redeposited on the surface. Usually the surface-active detergent compounds have a water-soluble portion (hydrophilic) and water-repellent portion (hydrophobic) in the same molecule. Ion-exchange mechanisms have been shown by McBain [1] to play an important part in the action of such detergents, and this author has discussed "solubilization" of hydrocarbons in water by the use of detergents. Thus, water and ionic reactions play an essential part in such a detergent operation. In hydrocarbons in the presence of suitable additives the "carbon" is dispersed throughout the liquid phase and settles very slowly so that a different mechanism is probably present, since no appreciable electrolytic action would be possible in the absence of water. In used oils, water is, however, present in at least small proportions and must be considered in connexion with the dispersivity of carbon in hydrocarbon solvents.

The present paper is put forward as a preliminary discussion on the way in which detergent additives behave in lubricating oils.

The carbon present in used lubricating oils from internal-combustion engines is partly derived directly from the fuel and lubricating oil as a product of incomplete combustion and partly by abrasion of carbon deposited in the engine in such parts as the piston-crown and cylinder-walls.

Detergent additives are used to maintain the carbon in suspension, but in order to consider the function of the additive, the resins and asphaltenes in used oils must also be considered.

Nature of Oil-decomposition Products.

The colloidal system of a used lubricating oil may be classified in three parts :—

(1) dispersion medium, consisting of the unaltered oil plus additive;
(2) protective colloids, such as oil soluble resins and asphaltenes formed as a product of decomposition of the oil;
(3) dispersed phase, of asphaltenes and " carbon."

The flow properties of the oil and the stability of the system will depend on the interrelation of these three parts.

The analysis of used lubricating oils is usually made by a series of solvents petroleum ether being used to precipitate the asphaltenes from the asphaltic resins and oil. The asphaltenes are filtered off and can be extracted by other solvents such as benzene and chloroform giving progressively smaller yields of the insoluble product. The asphaltic resins can be separated from the petroleum-ether solution of oil and resins by treatment with an active clay when the resins are preferentially adsorbed; by extraction of the clay with petroleum ether, the oil is removed, and the resins can be recovered from the clay by solution in chloroform or benzene or similar solvents.

Thus a series of products are formed ranging from hydrocarbons to so-called " carbon," and these are characterized by a progressive decrease in the hydrogen–carbon ratio, although oxygen compounds are also present. The used oil is formed by a process of oxidation which is partly oxygenation and partly dehydrogenation. In laboratory oxidation of oil with air or oxygen at elevated temperatures " carbon " is not usually formed, and hence it appears that the bulk of the " carbon " originates in other ways, mainly as sooty material formed by incomplete combustion of hydrocarbon fuel or of the lubricating-oil spray which is present in the combustion zone.

It is not possible to effect a sharp distinction between asphaltic resins and asphaltenes and carbon as these merge into one another, and chemical composition of these various products as determined by the same methods of analysis varies according to the proportions present.

The resins and the more soluble asphaltenes act as peptizing agents to maintain the more insoluble asphaltenes and " carbon," in colloidal suspension and as the proportion of asphaltenes increases, the oil becomes more viscous and at the same time becomes a gel. The character of the hydrocarbons is also of importance, and naphthenic oils with a higher solubility for asphaltenes may have a greater tendency to retain carbon in suspension. However, laboratory oxidations are usually carried out so as to give much larger proportions of asphaltenes and asphaltic resins than are present in used oils from internal-combustion engines. In consequence, the proportion present in used oils is not generally sufficient to have any great effect on the dispersivity of carbon, but the fact that products such as asphaltenes and asphaltic resins are present must be considered in the more general question of used lubricating oils.

The asphaltenes and carbon in the engine will adhere together giving solid sludge in the crankcase, etc., and additives may serve to prevent this coagulation in the same way as an emulsifier prevents the adhesion of the droplets of emulsified product. It is, however, mainly as a dispersing agent that the additives should be considered.

Previous Work.

Dispersions of Powders in Liquids.

The present knowledge on the behaviour of surface-active agents in the dispersion of powders in liquids does not appear to be sufficient to explain adequately the dispersion of carbon in hydrocarbon liquids.

The dispersion of titanium-dioxide, zinc-oxide, and zinc-sulphide pigments in non-aqueous liquids such as benzene was studied by Ryan, Harkins, and Gans.[2] The pigment suspensions were allowed to settle under gravity, and the final apparent (sediment) volume of the pigment was recorded as the sedimentation volume. The sedimentation volumes of titanium dioxide and other pigments were determined in a range of liquids of varying degrees of polarity. When the liquids were arranged in the decreasing order of the sedimentation volumes occupied by titanium dioxide it was found that they were also in order of increasing polarity of the liquids. Thus, the pigment occupied the greatest sedimentation volume in non-polar liquids such as heptane or benzene and the smallest in polar liquids such as aniline or methanol. This relationship was found to apply also to the other pigments tested.

Analogous behaviour was found on measuring the heats of immersion of the dry powders in pure liquids; the heat of immersion was least when no polar group was present, and increased with the polarity of any active group present in the organic molecule. It is further stated that if the liquids are arranged in increasing order of their heats of immersion with respect to one pigment they are found to be in the same order with respect to any other pigment. The pigments used in the heats-of-immersion experiments were titanium oxide, stannic oxide, silica, and barium sulphate.

If titanium-oxide pigment is dispersed in a volume of a non-polar liquid such as benzene, then it will occupy a large sedimentation volume. If, however, it is dispersed in the same volume of benzene to which has been added a low concentration of oleic acid, then the sedimentation volume of the pigment is greatly decreased. The presence of a $2{\cdot}5 \times 10^{-4}$ molar concentration of oleic acid was sufficient to reduce the volume of a suspension of 8 g of pigment in 50 cc of benzene to less than half that of the sedimentation volume in pure benzene. Compounds similar to oleic acid (in that both polar and non-polar groups were present—so-called polar–non-polar compounds—gave similar results. Examples are metallic soaps such as aluminium and titanium stearate, lead and cobalt naphthenate. Generally there was found to be an optimum concentration for the polar–non-polar compounds above which no further change in the sedimentation volumes could be detected, but this concentration varied with the different solutes, an observation which was confirmed by Damerell and Urbanic.[3] Earlier work on the adsorption of oleic acid from benzene by pigments showed that the adsorbed film on the surface of the pigment probably does not become

thicker than monomolecular. It was suggested by W. D. Harkins and D. M. Gans [5] that the function of this adsorbed film is to act as a lubricant to assist in the closer packing of the particles.

From all the evidence on dry suspensions put forward by Ryan, Harkins, and Gans, it appears that the decrease in sedimentation volume caused by the presence of a low concentration of oleic acid in benzene is directly associated with the amount of oleic acid present, and is due to the adsorption of a monomolecular film of oleic acid round the particles. At least there is no definite evidence that more oleic acid is adsorbed than can be accommodated on the pigment surface in one layer (specific areas determined by nitrogen adsorption).

Effect of Water.

The heat of immersion of titanium oxide in benzene increased with increasing proportions of water in the benzene up to a maximum which corresponds closely to the heat of immersion of the same pigment in water alone.[2] The general effect of the presence of water in pigment suspensions in the various liquids was to cause an increase in the sedimentation volume, this effect being most marked among the non-polar liquids and least in liquids having highly polar molecules. When small amounts of water are added to a suspension of titanium oxide in benzene containing oleic acid the sedimentation volume increases with the proportion of water. With a fixed proportion of water the sedimentation volume increases with the decrease in the proportion of oleic acid present. Further work using instead of oleic acid the metal soaps in benzene produced similar results.

Since pigments in both oleic acid and water have high heats of adsorption, both of these liquids wet the pigments satisfactorily. Both oleic acid and water gave low sedimentation volumes with all pigments tested. Yet when water is added to a suspension of pigment in benzene the sedimentation volume is greatly increased, whilst on the addition of oleic acid to a similar suspension, the sedimentation volume is greatly decreased.

In this work it will be noted that the pigments used are wetted with water and the general result obtained by the use of surface-active agents is to give lower sedimentation volumes, *i.e.*, less dispersion of the pigment than is obtained in the pure hydrocarbon.

Damerell and others [2,6,7,8] investigated the effect of surface-active agents on carbon black and litharge, which are presumably not readily wetted with water. (They also included silica and calcium carbonate which should be more readily wetted with water than hydrocarbons, and this will be discussed later.) The surface-active agents used were metal soaps and organic amines with xylene as the non-aqueous liquid.

The degree of dispersion was measured by the settling rate of a suspension of 0·5 g of the powder in 500 cc of xylene. In the case of the carbon-black suspensions, this rate was greatly decreased by the addition of certain surface-active agents, thus indicating the presence of greater numbers of particles in the smaller size groups. The most effective surface agents were copper oleate, cobalt naphthenate, and sodium dioctylsulphosuccinate. These were found to be positively adsorbed on the carbon black, as the concentration of the surface-active agent in the solution was lower after the carbon black had been added. When, on the other hand, oleic

acid was employed as the surface-active agent, it was found to have no measurable effect upon the degree of dispersion of the carbon, and furthermore to remain unadsorbed. For the effective surface-active agents an optimum concentration was observed, above which no further increase in dispersing power took place; for 0·5 g of carbon black in 500 cc xylene this occurred with the low concentration of 0·001 mol of surface-active agent.

Experiments with the same surface-active agents were made with dispersions of calcium carbonate, silica, and litharge in xylene with very similar results, *e.g.*, sodium dioctylsulphosuccinate was also effective in dispersing calcium carbonate whereas oleic acid was not. For all the surface-active agents the suspensions were found to be most stable and the active agents to have the greatest effect under conditions of extreme dryness.

Thus the work of Ryan, Harkins, and Gans indicates that the decrease in sedimentation volume is directly associated with the proportion of oleic acid present and is due to the adsorption of a monomolecular film of oleic acid around the particles; the monomolecular film calculation is based on the surface area as determined by nitrogen adsorption. The effect of the surface-active agent with these hydrophilic pigments is to increase the rate of settling, although the presence of the absorbed layer would prevent them coagulating together, so that further dispersion could be easily accomplished by shaking.

Damerell and Urbanic found with hydrophobic pigments, such as carbon black, that the surface agents they used (one of which, cobalt naphthenate, was the same as one used by Harkins *et al*) decreased the rate of settling. Oleic acid, with these pigments had no effect and was not absorbed to any appreciable extent. Damerell and Urbanic report, however, similar effects with calcium carbonate, which should be easily wetted with water.

It is difficult to reconcile these results. McBain [1] in discussing non-electrolytic detergents in aqueous media points out that they cannot be considered as colloidal electrolytes and that little is known of their action. In non-aqueous media, the surface-tension curves, as for example, of lauryl sulphonic acid in mineral oil, show a rapid drop in surface tension with relatively small concentration and a minimum followed by a slow rise; he interprets this to mean that an electrical double layer is present, probably of the Helmholtz type. He thus considers that such additives in non-aqueous media can solubilize and peptize the sludge present, serving to keep the engine clean. On this basis the suspending action of the additives would be as follows. A charge is imparted to the carbon particles so that charges of opposite sign remain near the particles through electrostatic action. When the carbon particles tend to settle they carry with them the associated free ions. The effective weight of the particle is the average of the particles plus the ions, and hence is substantially the same as that of the particles themselves. Owing to the larger volume, however, due to the associated free ions, the rate of settling is very much lower.

Present Work.

Experimental.

It was decided to investigate the dispersion of carbon black in toluene by observing its rates of settling with various additives. Carbon black

can be obtained in a series of known sizes, and for most of this work Micronex of an average particle size of 30 mμ was employed.

The "carbon" in used oils is essentially different in character from carbon black, owing to the associated asphaltenes. The size of the "carbon" in used lubricating oils must vary widely, but a figure has been given of 0·25 μ by McNab *et al.*[9] Even in carbon black there are present compounds other than carbon, so that it is not by any means a pure substance. Before use the carbon black was extracted in a Soxhlet apparatus with toluene and dried *in vacuo* at 70° C.

In this investigation it was intended to use a series of relatively simple additives such as calcium soaps, and then to investigate soaps of other alkali earths, and later soaps in which various substitutions have been made, such as chlorine or sulphonic acids. Some limitation is imposed on the type of soap used by its solubility characteristics in toluene, and in the initial experiments, calcium naphthenate was used. This was made from a fraction of naphthenic acid of molecular weight 190, which was separated from other napththenic acids by fractional distillation under vacuum.

Dispersion of Carbon Black in Toluene.

It was considered of some importance to break up the agglomerates of carbon black as completely as possible in order to obtain a fine dispersion of the carbon black in toluene. Comparison was made between the rate of settling of carbon black in toluene when mixing was effected by the following methods :—

(*a*) mixing by means of ultrasonic waves as described later;
(*b*) stirring with an electric motor;
(*c*) vigorous shaking by hand.

The three suspensions so obtained gave a marked difference in the rate of settling and are illustrated in Fig. 1, which shows that volume of the carbon black in (*c*) occupied approximately twice that obtained by simple shaking method (*a*). This corresponds to a particle size of about 1½ μ, namely approximately fifty times that of the particles present in the Micronex. These experiments, however, were made with a suspension of 2½ g in 100 cc and under these conditions free settling cannot occur.

Preliminary experiments have shown that a suspension vigorously shaken by hand gives a minimum particle size of 10 μ as compared with 6 μ obtained by stirring with an electric motor. Attempts were made to reduce the particle size by stirring by means of a moving-coil radio-type loudspeaker, to the paper diaphragm of which was attached a light aluminium piston. This system was found capable of giving vibrations of 50 cycles per second in the carbon-black suspension and a minimum particle size of 3·5 μ was obtained.

Many instances have been reported of the ability of supersonic waves to produce fine emulsions and dispersions, as they have also of their ability to produce the opposite effect, the coagulation of aerosols and dispersions in liquid media. It would appear that the difference lies in the intensity with which the sound is propagated, up to frequencies of approximately 1 Mc. If the intensity of the wave is low and standing wave patterns are set up, then these are the conditions for coagulation, and particles will

collect at the antinodes of the standing wave. If, however, the intensity is high enough for the occurrence of cavitation in the liquid, then the cavitational forces—the formation and collapse of bubbles—will produce the dispersive forces which break down agglomerates of particles.

Experiments to construct a quartz oscillator with a frequency of 1 Mc did not give enough power to produce satisfactory results, and accordingly a magnetostriction oscillator using a nickel tube was constructed. This produced sound waves at a frequency of 19 kc. A radio-frequency oscillator (Hartley circuit) capable of being tuned to a frequency of 19 kc drives a nickel tube (cut to have a fundamental frequency (longitudinal vibration) of 19 kc), and polarization of the tube was obtained with a strong electromagnet. The oscillator circuit is shown in Fig. 2.

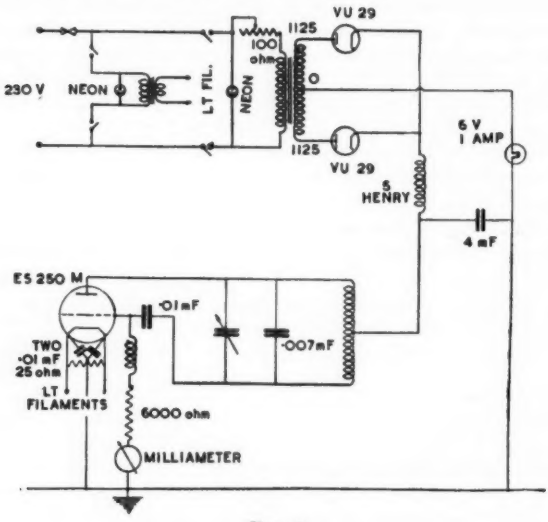


FIG. 2.

MAGNETOSTRICTION OSCILLATOR.

The supersonic waves produced by this apparatus are capable of very powerful dispersive actions on small volumes of liquid. They will produce an emulsion of toluene in water which is stable for about 20 hr, and can also emulsify mercury and water—although this emulsion will not be stable for much more than an hour. When a suspension of carbon black in toluene was prepared by this means under the same conditions as the other dispersions, the minimum particle size was 1·5 μ in pure toluene. It is apparent that the use of supersonic waves was the most effective of the methods of dispersion reviewed.

Determination of the Rate of Settling.

Reference has already been made to the methods used by Harkins and Damerell for determining the rate of settling of powders in non-aqueous liquids.

The systems which we investigated were relatively dense suspensions of carbon black in toluene, and these were preferred for two reasons :—

(1) It was hoped to obtain experimental evidence of the interrelation of the particle surfaces, possible adsorbed layers and the dispersion medium from the rates of settling.

(2) It was desired to find out as accurately as possible the proportion of additive adsorbed on the carbon surface; for this purpose relatively dense suspensions were preferred as these would absorb more additive and this was important in view of the difficulties in estimating the proportion of additive present.

For most of our work we determined the rate of settling by determining the sediment volume over a period of time until no further alteration in volume took place. Graduated 25-cc cylinders of the same diameter were used, and the settlings were observed under controlled-temperature conditions.

An apparatus was also devised for the automatic recording of particle-size determinations in which an aluminium pan (of 1·5 cm diameter) was suspended in the carbon-black–toluene solution. This was suspended from a light rod fixed to a torsion wire on which was a mirror. The position of the pan could thus be determined, and its movement recorded by an optical-lever system focused on a revolving drum covered with light-sensitive paper. In this way curves were obtained of the rate of settling over a period of 24 hr under controlled-temperature conditions. This apparatus, however, was subject to two possible errors : (*a*) the carbon settling on the pan would not necessarily be only that present in the cylindrical volume above it; and (*b*), as the pan descended in the carbon-black suspension, some agitation was inevitably caused.

In the method finally adopted, the volume occupied by carbon particles could be plotted against time, and thus not only the final sediment volume obtained, but also the rate of settling. As will be seen later, the rate of settling is not usually a straight line, since the larger particles settle out first with a relatively high rate of settling, and the finer particles settle more slowly later giving a lower rate of settling. It should be noted that the upper surface of the carbon suspensions used was quite sharp so that progress of settling could be clearly followed.

Determination of Additive.

In the determination of the amount of calcium naphthenate present in the toluene solution, attempts were made to use the conventional methods of analysis. Calcium soap was decomposed with concentrated hydrochloric acid, giving a solution of calcium chloride. This was evaporated to dryness and the chloride present determined by titration against $N/50$ silver-nitrate solution using potassium chromate as indicator. These methods were not sufficiently accurate to determine the small changes in concentration which occur due to the adsorption of additive on the carbon black. Accordingly, a method of analysis by physical means was developed using the Langmuir trough. In the method adopted, a known quantity of the solution was placed on the surface of water in the trough, the solvent allowed to evaporate, and the force-area curve developed.

Substances which are insoluble in water may under favourable circumstances be spread as films of monomolecular thickness on a water surface. When subjected to compression these films show characteristic force-area curves (the force exerted against a moveable barrier may be measured for example by a torsion wire). The compressive properties of these films depend upon the relative attraction which molecules have for adjacent molecules in the film and for the aqueous substrate. The films are classified in three main groupings according to the nature of their force-area curves

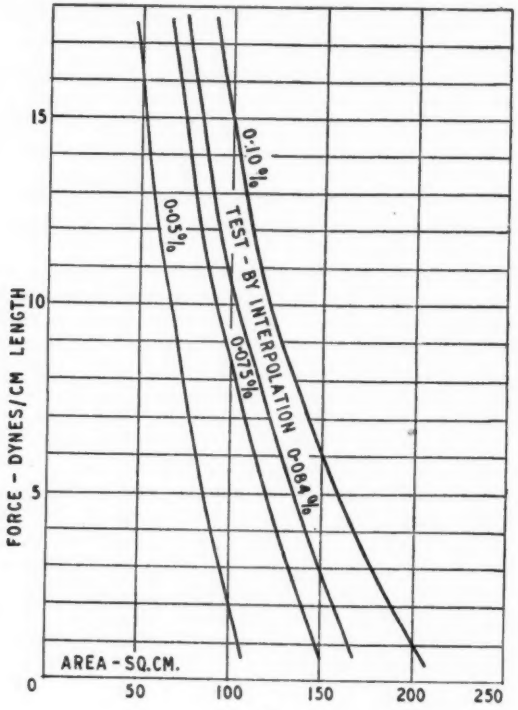


FIG. 3.

as condensed, liquid-expanded, or gaseous films, a detailed description of which has been given by Adam.[10]

It was found that calcium naphthenate formed films of the liquid-expanded type when spread upon a distilled-water surface.

Accurately measured equal volumes of calcium-naphthenate solution in toluene of varying concentrations are in turn spread upon the clean water surface of a Langmuir trough and the toluene allowed to evaporate. It was found that the required accuracy of delivery was best made by means of the Harkins-type micropipette [11] (volumes of 1/50 to 1/30 cc). The force-area characteristics are determined for each of these solutions by the nul-displacement method, *i.e.*, the movable barrier is brought back to a

fixed position by the torsion wire for each reading. If the concentrations of the solutions examined lie fairly close together the force-area data may be plotted on one graph for comparison. It is found that the curves are identical in shape but displaced along the area axis depending upon the concentration differences. Fig. 3 shows a graph of the force-area curves of solutions employed in an experiment to determine the amount of adsorption. From such a graph it was found possible to determine the concentration of calcium naphthenate in unknown solutions by interpolation when the force-area curves are plotted in this manner together with curves of standard reference solutions. The displacement along the area axis is found to vary in a linear manner with concentration.

Materials Used.

Carbon Black. Standard grade of Micronex—mean particle size rated as 28 mμ. Before use, the Micronex was extracted with toluene in a Soxhlet apparatus and dried at 70° C in a vacuum oven for 12 hr over barium perchlorate. It was desired to free the carbon black as completely as possible from water.

Toluene. A.R. grade was employed.

Additive Calcium Naphthenate. Prepared by double decomposition of sodium naphthenate with calcium chloride. Sodium naphthenate was obtained from a fractionated naphthenic acid, the equivalent weight of which was 190 (calculated from acid value).

One set of experiments were also made with calcium-naphthenate solutions to which a small proportion of water had been added.

Sedimentation Vessels. 25-cc graduated cylinders of matched dimensions.

Method. 0·5 g. of dried Micronex are dispersed in 20 ml of the liquid phase (pure toluene or a soap solution in toluene) by irradiating them for 2 min with ultrasonic waves. The suspension is then transferred to the sedimentation vessel, and 5 ml of the appropriate solution added in rinsings. The movement of the upper boundary of the suspension with time is then recorded. It should be noted that this boundary is quite clearly defined throughout the settling. After the final sedimentation volume was recorded, a sample of the clear solution above the suspension boundary was withdrawn for analysis on the Langmuir trough. The quantity of solute adsorbed on the Micronex was calculated from the force-area curve.

Comparison of Adsorptive Powers of Black.

A comparison was made of the adsorptive capacity of two carbon blacks and showed higher adsorption for the carbon black of smaller particle size.

1 g Thermax . . . average size 0·3 μ
1 g Micronex . . . ,, ,, 0·028 μ
1 g of each dispersed in 20 ml 0·01 per cent calcium naphthenate.
1 g Thermax adsorbs 0·16 mg calcium naphthenate
1 g Micronex adsorbs 0·54 mg calcium naphthenate.

Adsorption of Calcium Naphthenate on Carbon Black.

The exact nature of the adsorption isotherm for the adsorption of

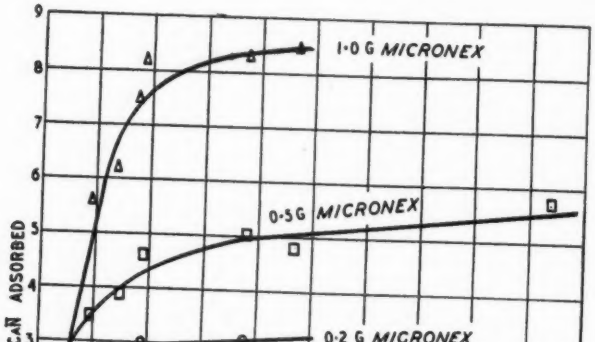

1·0 G MICRONEX
0·5G MICRONEX
0·2 G MICRONEX
0·1 G MICRONEX
MG CAN ADSORBED
CONCENTRATION – G CAN/100 CC TOLUENE
0
1
2
3
4
5
6
7
8
9
0·1
0·2
0·3
0·4
0·5

FIG. 4.

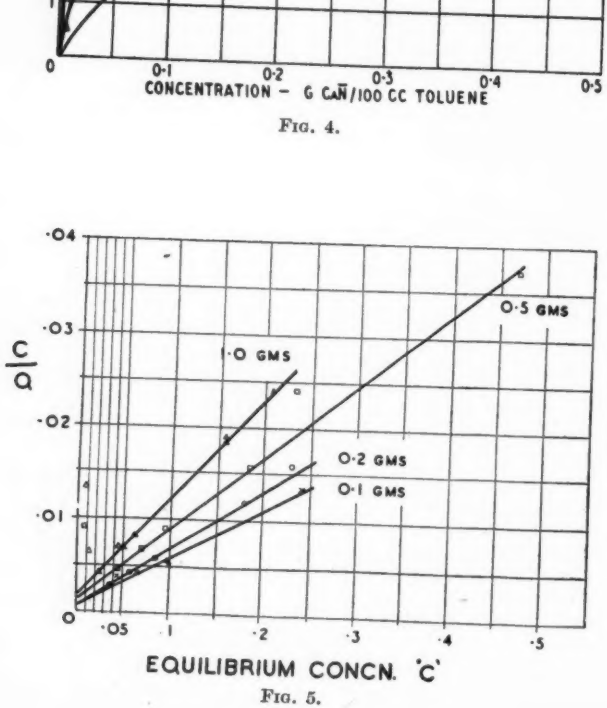

·04
·03
·02
·01
0
x/c
1·0 GMS
0·5 GMS
0·2 GMS
0·1 GMS
·05
·1
·2
·3
·4
·5
EQUILIBRIUM CONCN. 'C'

FIG. 5.

solute from solution is still uncertain. It is generally thought that adsorption proceeds until the formation of a " monolayer " on the adsorbing powder—this being indicated by the saturation value reached. However, a recent paper by Ying Fu, Hansen, and Bartell [12] argues the existence of second and third adsorption layers, and this is supported by experimental evidence on the adsorption of butyric acid on graphite from aqueous solution.

It does appear certain that such adsorption layers as are formed, whether first, second, or third layers, are not the completed monolayers that are found in gas-adsorption experiments, but represent an equilibrium on the particle surface between solute and solvent molecules, both of which are in contact with the surface of the particle. Thus the area which can be calculated from the solute-adsorption data is probably much farther from the truth than an area calculated from nitrogen-adsorption isotherms and cannot readily be correlated with the true surface area. The nitrogen surface area includes most of the surface of the pores present in the particles, and the finer pores cannot be penetrated by large molecules such as additives. Therefore, the area covered by a unimolecular layer of additive may be much smaller than that measured by the nitrogen surface area.

A series of experiments were made with 0·1 to 1·0 g of Micronex per 25 ml of calcium-naphthenate solution ranging from 0·0094 to 0·47 per cent. The results are given in Table I and Figs. 4 and 5. These results show that the adsorption of calcium naphthenate by Micronex from toluene solutions follows the Langmuir equation up to a concentration of 0·47 per cent ($11{\cdot}1 \times 10^{-3}$ M). The apparent disagreement below 0·0234 per cent ($0{\cdot}55 \times 10^{-3}$ M) concentration is probably due to greater inaccuracies in measuring adsorption at these low concentrations.

TABLE I.

Mg of Calcium Naphthenate Adsorbed.

Concentration of calcium naphthenate solutions, per cent.	Weight of Micronex in 25-ml toluene solution of calcium naphthenate.			
	0·1.	0·2.	0·5.	1·0.
0·0094	—	—	—	0·54
0·0235	—	—	—	2·2
0·047	1·2	2·8	3·5	5·6
0·0705	1·5	2·7	1·9	6·2
0·0822	—	—	—	7·5
0·094	1·7	3·0	4·6	8·2
0·188	1·8	3·1	5·0	8·3
0·234	1·7	2·9	4·8	8·5
0·47	—	—	5·8	—

Saturation values are reached for each concentration of Micronex in 0·188 per cent ($4{\cdot}44 \times 10^{-3}$ M) solutions. When the $\frac{x}{m}$ values (mg of calcium naphthenate adsorbed per g of Micronex) are calculated from these saturation values $\frac{x}{m}$ is found to decrease with the increase in Micronex concentration (Table II).

TABLE II.

	0·1 g.	0·2 g.	0·5 g.	1·0 g.
$\frac{x}{m}$	18	15	11	8·5

Sedimentation Volumes and Settling Rates.

A series of suspensions of Micronex in toluene solutions of calcium naphthenate were made containing 0·5 g of Micronex in 25 ml of toluene; the calcium-naphthenate content varied from 0·0094 to 0·47 per cent. The sedimentation volumes were recorded initially at 15-min intervals up to 2 hr, later at longer intervals up to a total of 48 hr, when in all cases it was found that no appreciable decrease in the sedimentation volume took place. A number of blank determinations were made with no calcium naphthenate present. In one or two instances difficulty was experienced in obtaining satisfactory dispersion, owing to low voltage on the ultrasonic

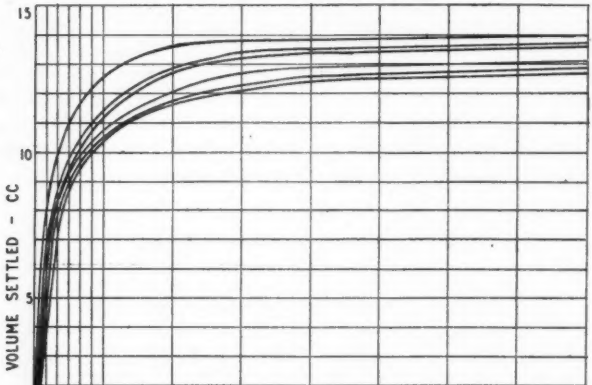


FIG. 6.

apparatus, and these results have been omitted. The curves for the blank determinations are shown in Fig. 6, which shows that in some cases unsatisfactory dispersion was effected. The curves show a fairly rapid settling in the initial period up to about 3 hr, during which time the coarser particles settled out; the finer particles settled at a much slower rate during the remaining period. The average final sedimentation volume of these experiments was 11·8 ml. For the 0·0705 per cent calcium-naphthenate solution, Fig. 7, it will be seen that the two results repeated one another fairly closely, but again showing a slight falling off in the rate of settling with increase in time. Similar results for a more concentrated solution 0·47 per cent

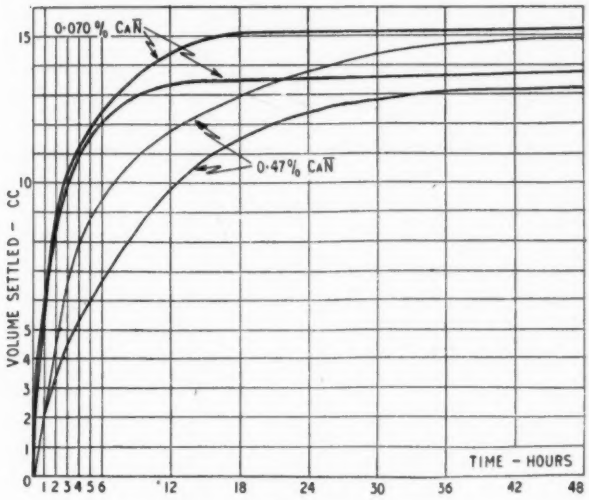


FIG. 7.

calcium naphthenate show a more uniform rate throughout. Thus, the presence of increased proportions of calcium naphthenate results in a much more uniform rate of settling corresponding to better dispersion in the presence of adsorbed additive.

Table III summarizes the results obtained. In Column 1 is given the concentration of calcium naphthenate in g/100 ml. Column 2 is the volume of clear liquid above the carbon sediment after 3 hr; Column 3 the volume after 48 hr, *i.e.*, total settling; Column 4 shows the ratio of the settling over the last 45 hr as compared with that over the whole 48 hr; and Column 5 the average of these ratios for each of the concentrations employed.

As already pointed out, the coarser particles settle out first and the fine particles more slowly. With increased concentrations of calcium naphthenate there are fewer coarse particles present, as indicated by a more uniform rate of settling throughout the 48-hr period. It was therefore decided to use the rate of settling of the finer particles as an indication of the degree of dispersion. The 3-hr initial period was chosen because of the results when no calcium naphthenate was present, although perhaps a 1-hr period might have been more suitable for a comparison of the degree of dispersion with increasing proportions of additive. The results shown in Column 5, Table III, indicate a steady improvement in the degree of dispersion with increasing concentration, except that the average of the blank determinations gave a better dispersion than was obtained with concentrations of calcium-naphthenate solution below about 0·05 per cent concentration.

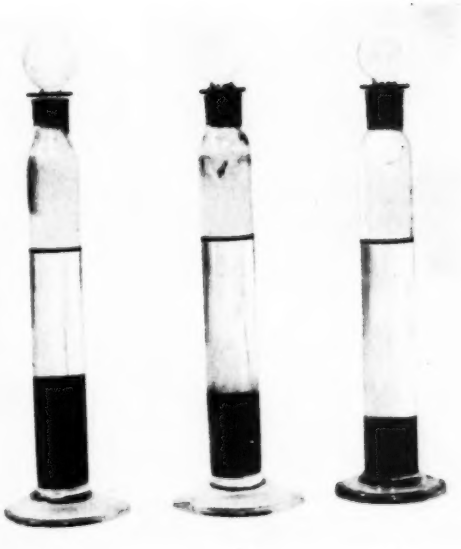
Table IV for the same concentrations shows the adsorption of calcium naphthenate on Micronex. Column 2 gives the mg of calcium naphthenate adsorbed; Column 3 the percentage adsorption of calcium naphthenate;

TABLE III.

Conc of solution, g/100 ml.	Settling in 3 hr.	Total settling in 48 hr.	Percentage Settling 3–48 / Settling 0–48	Average percentages 3–48 / 0–48 hr.
(1)	(2)	(3)	(4)	(5)
Blank 1	9·0	12·4	27·4	
2	10·0	13·8	27·6	
3	10·0	13·8	27·6	
4	9·0	12·8	29·6	26·7
5	8·8	12·6	30·0	
6	10·2	12·8	20·5	
7	10·5	14·0	25	
0·0094	11·2	13·7	18·3	18·3
0·047	11·9	14·6	18·5	
	12·8	14·9	14·1	23·5
	9·1	14·7	38·0	
0·0705	10·0	15·3	35	32
	9·8	13·7	29	
0·094	9·5	15·0	37	
	11·4	14·8	23	
	9·6	15·4	38	32·25
	7·0	13·1	52	
	10·5	15·3	31	
0·188	5·9	14·3	58·5	62·5
	4·4	13·2	66·5	
0·234	6·3	13·8	55·0	55
0·47	4·5	13·0	65·0	62
	6·1	14·7	59·0	

TABLE IV.

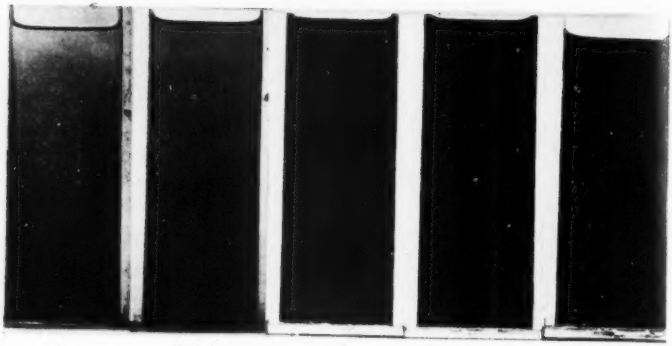
Conc of solution g/100 ml.	Mg $Ca\bar{N}$ adsorbed.	$Ca\bar{N}$ adsorbed/ total per cent.	c, equilibrium conc.	$\frac{q}{x/m}$ Mg $Ca\bar{N}$ adsorbed/g Micronex.	$\frac{c}{q}$
(1)	(2)	(3)	(4)	(5)	(6)
No detergent	—	—	—	—	—
Blank	—	—	—	—	0·0000
0·0094	0·421	18·0	0·0077	0·84	0·0009
0·047	3·37	28·9	0·0334	6·74	0·0049
	3·56	30·0	0·0327	7·12	0·0047
	3·47	29·5	0·033	6·94	0·0047
0·0705	4·03	23·0	0·054	8·06	0·0067
	3·84	22·0	0·0553	7·68	0·0072
0·094	4·22	18·0	0·0770	8·44	0·0091
	4·30	18·4	0·077	8·60	0·0090
	4·30	18·4	0·077	8·60	0·0090
	4·2	17·9	0·077	8·4	0·0092
0·188	5·1	10·7	0·168	10·1	0·0153
	5·1	10·7	0·160	10·1	0·0147
0·234	4·5	7·7	0·216	9·0	0·024
0·47	5·8	4·7	0·446	11·6	0·0384
	5·8	4·7	0·446	11·6	0·0384



a *b* *c*

FIG. 1.

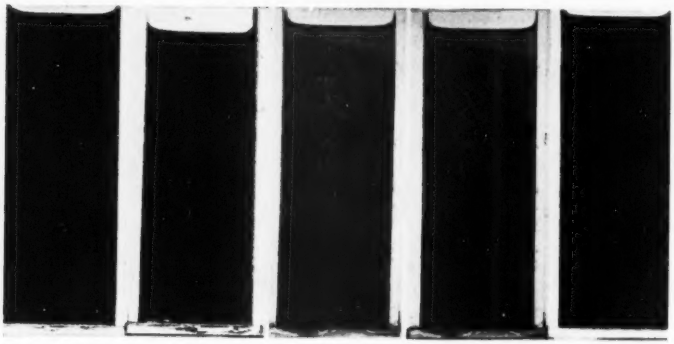
[*To face p.* 156.



0 0·003 0·01 0·03 0·10

Percentage of Ca soap added.

FIG. 9.



0 0·003 0·01 0·03 0·10

Percentage of Ca soap added.

FIG. 10.

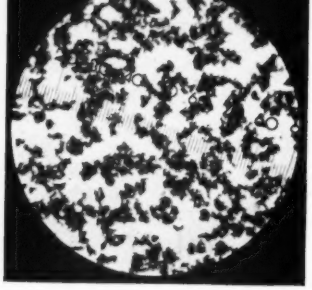


FIG. 11.

Column 4 the equilibrium concentration of calcium naphthenate after adsorption, *i.e.*, c in the Langmuir equation :—

$$q = \frac{aq_0c}{1 + ac} \text{ or } \frac{c}{q} = \frac{1}{a} + \frac{c}{aq_0}$$

where a and q_0 are constants; Column 5, mg of calcium naphthenate adsorbed per g of Micronex, *i.e.*, q in the Langmuir equation; Column 6 the ratio of c/q.

The results as regards adsorption in Table IV are plotted in Fig. 5, showing satisfactory agreement with the Langmuir equation.

Table V and Fig. 8 give a comparison of settling rate against mg of calcium naphthenate adsorbed per g of carbon black. In general there

TABLE V.

Conc of solution, g/100 ml.	Average settling rate, $\frac{3\text{–}48}{0\text{–}48}$ hr.	Average of calcium naphthenate adsorbed per g of Micronex, mg.
0	28·4	0
0·0094	18·3	0·84
0·047	23·5	6·9
0·0705	32	7·8
0·94	32·25	8·5
0·188	62·5	10·1
0·234	55	9·0
0·47	62	11·6

is an improvement in the settling rate, *i.e.*, degree of dispersion with increasing concentrations of calcium naphthenate, and this corresponds to increased adsorption of calcium naphthenate on the carbon black. When the concentration of 0·188 per cent calcium naphthenate is reached, there is little improvement in degree of dispersion, and this corresponds with an approach to saturation in the adsorption of calcium napthenate on the carbon black. Thus, the optimum concentration of calcium naphthenate is in the neighbourhood of 0·188 per cent. From Table I it will be noted that the maximum adsorption is reached at about this concentration for Micronex dispersions containing from 0·1 to 1·0 g Micronex per 25 ml of solution. If the results in Tables III and IV are confirmed by further experiments, it may offer a method of determining the minimum concentration of additive to give maximum dispersive power, by a simple adsorption test in which the maximum adsorption of additive is determined as in Table I.

The degree of dispersion with no detergent was better than that obtained with low concentrations of calcium naphthenate, but it will be noted that with the blank, there were present coarse particles as shown by the rapid initial rate of settling; repeat determinations were more widely different with the blank than with those experiments in which calcium naphthenate was present. The carbon particles have been found to be negatively charged, and the settling rates will be influenced by the extent of the electric charge, but the settling rates for carbon particles with adsorbed

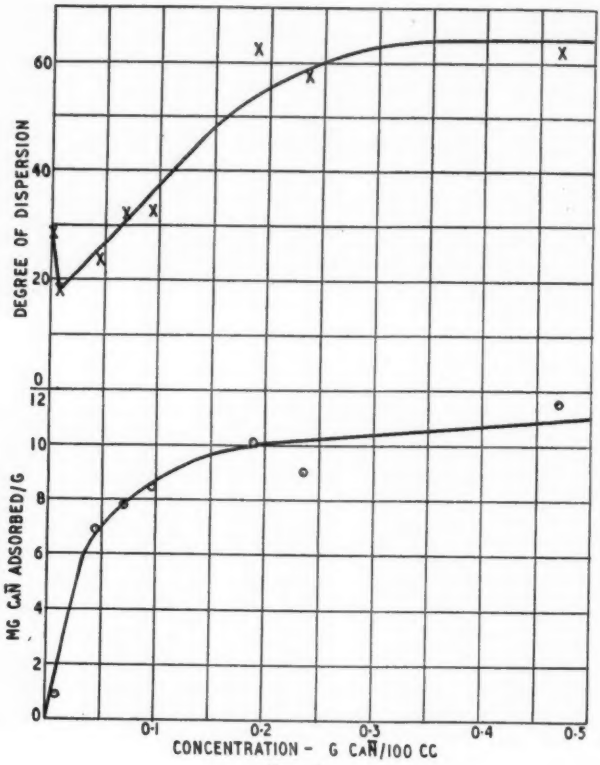


FIG. 8.

calcium naphthenate may be less affected by this charge than in the blank experiments.

Addition of Water to Calcium Naphthenate–Toluene Suspensions of Micronex.

Rates of settling were made on three concentrations of calcium naphthenate–toluene solutions (0·0705, 0·094, and 0·188 per cent) containing 0·5 g of Micronex per 25 ml of solution, to which had been added 0·037 g of water.

The results were erratic in that a clear solution was not obtained on settling the 0·094 and 0·188 per cent calcium-naphthenate solutions, and fine carbon particles were present. With the 0·0705 per cent solution, the wet solution gave slightly slower rates of settling than the dry solution.

Direct Measurement of Detergency.

A number of experimental tests for detergency have been described by Talley and Larsen [13]—filtration, infra-red, centrifugal, and chromatographic

detergency tests—but none of these appear to be wholly satisfactory. A preliminary sorting method has been developed using microscope glass slides as follows. Glass microscope slides have been placed in Micronex suspensions in toluene with varying concentrations of detergent and allowed to drain. The number of particles adhering to the slide has been determined as a blackness factor—measured by the light-absorption factor of the slide in a simple photo-cell system.

It was shown experimentally that the presence of the detergent in the dispersion reduces the amount of carbon black present on the slide. Over the range of concentrations examined, $0 - 1{\cdot}2 \times 10^{-3}$ m of calcium naphthenate, the cleanliness increases with increasing concentration.

Test Procedure.

Two suspensions were prepared of 0·5 g of carbon black in 25 ml toluene and in two concentrations of calcium naphthenate. After the supersonic mixing they were stirred occasionally with a glass rod until restored to room temperature.

The glass microscope slides were chemically cleaned and dried, and immediately before use held above a flame until the moisture film had evaporated. They were wetted first with a solution of calcium naphthenate (of the same concentration as that of the carbon suspension tested) and then held in the carbon suspension for one minute with no stirring. The slides were then withdrawn and allowed to drain rapidly in contact with filter paper. One side of the slide was wiped clean and the light-absorptive power of the centre of the covered part of the slide examined in the photo-cell system.

Table VI shows the averages of three readings for each of these solutions in toluene.

TABLE VI.

Conc of $Ca\bar{N}$ solution.	Light absorbed, per cent.	
	A.	B.
No detergent . . .	35	15·0
$0{\cdot}95 \times 10^{-3}$ m . . .	25·5	12·5
$1{\cdot}9 \times 10^{-3}$ m . . .	22·5	10·0

TABLE VII.

Conc of $Ca\bar{N}$ solution.	Light absorbed, per cent.	
	A.	B.
No detergent . . .	56·5	25
$0{\cdot}95 \times 10^{-3}$ m . . .	46·1	15
$1{\cdot}9 \times 10^{-3}$ m . . .	44·0	12

Suspensions A and B were allowed to settle for 24 hr and then stirred again—this time only with a glass rod—and the experiment repeated.

It is seen that each suspension gives a dirtier slide than it did previously (Table VII). These results show an improvement with the low concentration of additive as would be expected in comparison with that obtained with no additive.

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Discussion.

The President (Mr E. A. Evans): We have had a wonderful illustration of the exquisite working of the mind when it is in an academic environment. Most of us, I think, would be content to shake a bottle with materials in it. But not so will the man who has an academic mind; he resorts to the most violent methods and adopts methods such as supersonic wave motion. I think that is a most wonderful way in which to shake a bottle. I wonder what would have happened if they had had the atom-breaking machine at Birmingham at their disposal. Would they have removed the intermolecular forces? Then the experimental work would not have been worth a hoot!

However, we must realize that we are dealing only with Part I of a series of papers; we have had simply an introduction to the subject.

We have to ask ourselves, where is all this leading? What is the ultimate outcome of it all? Clearly those of us who are interested in this subject are being faced with enormous expense due to the fact that we have not the means in the laboratory for determining the values of these additives. We are compelled to use engine testing; engine testing is tedious, requires an enormous amount of standardization, which is expensive. I think we should be pleased to have something else to take its place. The firms who have already installed engine-testing laboratories would possibly be faced with a little labour difficulty, now that they have the staffs already installed, if it were found that the academic people were pushing them out of a job. But that is a trouble we can deal with when it arises. We have to concentrate on the paper this evening.

I suppose that most of us have our idiosyncracies; one of mine is that when someone describes a deposit in an engine as carbon I feel a little disquieted, because I am not yet convinced that there is any carbon—or at

least very little—in these deposits. I am not convinced that the carbon–hydrogen ratio is precisely as Mr Baddeley has suggested. In our own work, by a series of extractions, we have found that the oxygen content always goes up, which complicates the issue. The authors of the paper were cautious, however, in putting the word " carbon " in inverted commas, for apparently they are not sure just how they should describe it.

It is not for me to ask why the authors chose calcium naphthenate; there may be some subtle reason for it, but it would be interesting to know. The authors are dealing with a problem of great academic importance. McBain and his co-workers have done a lot of work on the solubility of soaps and their behaviour in aqueous media. Now we are faced with the problem of the solubility of metal soaps and organic metal salts in hydrocarbon solvents. Harkins has done a certain amount of work and, of course, there are others, perhaps lesser known. They have all been faced with this great difficulty of what happens in so-called solution. We feel that it is not strictly a solution, but something else, which serves to complicate the issue.

When carbon black is suspended in a hydrocarbon fluid and some adsorption takes place, one naturally asks how that adsorption occurs. Is it a uni-molecular layer or is it some complex layer that is formed? Does it form evenly or does it form on certain nuclei? All these difficulties complicate the subject under discussion. This evening we have a great opportunity to cross-examine the three gentlemen who are responsible for the paper. We have the heavyweights here, so that you need not be afraid to put questions.

We have with us this evening two Fellows from overseas, and we always like to give our friends from overseas a very hearty welcome. My very good friend M. Roegiers, from Ghent, is here; for the last thirty years his name has been associated with Elektrion, that material which is prepared by bombarding rape oil with electric energy. He is not here to tell us how it is done, but we do want to give him an opportunity to join in the discussion of the paper, for I feel sure he would like to make a contribution.

We have also with us Dr Van der Minne. I well remember him attending the General Discussion on Lubrication, organized by the Institution of Mechanical Engineers; he presented a paper. We are very glad to see him this evening.

M. M. Roegiers: I am glad to take part in the discussion because I have some experience of the " dispersing " properties described in this very interesting paper. When I say that I have *some* experience, I mean that I have been studying those properties theoretically and in practice for more than thirty years. Many of my observations are quite in agreement with the test results given in the paper.

For example, I have with me some bottles containing :—

(1) 0·5 per cent by weight of carbon black in toluene;

(2) 0·5 per cent by weight of carbon black in toluene, plus 2 per cent of a dispersing agent.

Formerly I had worked, not with toluene, but with fluid mineral lubricating oil—you call it 300 burning oil, I believe—and then I thought about

carbon black, and bought some in a shop. I put 0·5 per cent or so of it in the lubricating oil, and it went down rather quickly. Then I made the preparations with toluene. The first one, which consists of toluene with 0·5 per cent by weight of carbon black, was shaken only an hour ago, and already it has settled down to about ½-in at the bottom. Then the second sample, containing the same amount of carbon black plus 2 per cent of "Elektrion," does not show any sedimentation. In the first sample most of the carbon will settle out within an hour, whereas in samples of the second type there is no clear layer after they have stood for several weeks. In the sample of the second type which I have here you can see what appears to be a very small layer, being probably the larger particles of the carbon black: but there is no clear layer.

In all my work I do not use what the authors call "soaps"; and it is important to note that in the paper the authors place emphasis almost exclusively on "soaps". I use oils in which, we believe, the "directional forces" have been highly developed by some purely physical treatment; we believe we have proved that these forces are considerably developed by bombardment by electrons and nucleus.

These special oils contain no metallic radicles; therefore, they cannot themselves contribute "ash" at hot spots in an engine where, with any oil whatsoever, there is unavoidable decomposition.

The dispersing properties of mineral lubricating oils, containing small percentages of such electrically treated oils, are very striking indeed when their effect is observed on "soot" which comes to the oil in the course of its use in an internal-combustion engine.

Reverting to the paper itself, I do not see any reference to the solid matter other than carbon which is formed sometimes in relatively large amounts—I refer to the inorganic salts of lead from leaded gasolines. These also call for dispersion; and I would add that the dispersion properties illustrated by my second sample are also illustrated in a simple way for lead salts. I have with me a sample of used mineral oil to which has been added a small amount of the special additive. The oil has been used for a small mileage in a car using a gasoline leaded fuel. There are just very small lead particles which seem to be held in permanent suspension.

DR VAN DER MINNE: In the papers the authors refer to the peptizing action of oxidation resins. By oxidation resins we understand a group of oil-soluble oxidation products which are not precipitated by dilution of the oil with I.P. spirit and which are considered as the precursors of oxidation sludge which may be formed on further oxidation of the oil.

This oxidation sludge is insoluble in I.P. spirit.* The soluble oxidation resins impart a dark colour to the oil and increase the viscosity.

As already stated, these oxidation resins show peptizing action in a mineral oil. Metal soaps have this effect, too; in the paper this is shown for calcium naphthenate.

We have found that, curiously enough, when these peptizing agents are both present in certain concentrations coagulation may ensue. This

* The name "oxidation sludge" is preferred to the less discriminating name "asphaltenes"; see this *Journal*, 1948, **34**, 214.

coagulation is observed when mineral oil is the medium and also in the case of benzene; and it is found when carbon black or the insoluble sludge from used oils is the dispersed phase.

Figs. 9 and 10 illustrate these phenomena. Fig. 9 shows the behaviour of a suspension of lacquer-like material from engine tests dispersed in a fresh lubricating oil, with and without the addition of increasing amounts of a metal soap (calcium di*iso*propylsalicylate). It will be seen that 0·01 per cent of the calcium soap is necessary to cause peptization.

In Fig. 2 conditions are the same, except that instead of fresh mineral oil, the mineral oil is used in a slightly oxidized state.

In this case the oil without any metal soap shows peptization, whereas 0·01 per cent of Ca soap now brings about coagulation. A further addition of Ca salt causes peptization.

These results have been published in a paper * in which some reference is made as to electric charge as possibly playing a role.

THE PRESIDENT: Did you say that when you increased the calcium-soap concentration to a certain point, precipitation occurred, and when you increased the concentration still further, there was peptizing?

DR VAN DER MINNE: Yes, and this applies also the other way round. When you add oxidation resins to a suspension peptized with calcium soap you first get coagulation, and when you increase the concentration of oxidation resins still further you get peptization. In other words, when one of these two components is in excess, there is peptization, and when they are present in a certain ratio, there is coagulation.

MR L. GRUNBERG: We all realize the complications of the problem which the authors have attempted to attack. I think they have succeeded in isolating at least one section of the problem, and if it is not completely applicable to lubricating oils, there are other industries which are interested, foremost among them being the printing-ink industry, where carbon black forms an important ingredient. Those who have to deal with printing inks will be very grateful to the authors for their work.

We are grateful to the authors for their use of the Langmuir trough as an analytical tool. Many of us who venture into the field of applied physical chemistry will appreciate that innovation.

I should like to comment on the method of dispersion which has been used. I believe that the use of supersonic equipment for obtaining carbon-black dispersions was quite unnecessary; we have in our laboratory some experience of carbon-black dispersion, and we are using a device which has been known for centuries—for the alchemists used it—namely, the pestle and mortar. The dispersions obtained by this means are of the same degree of dispersion as by other means; indeed, at 450 magnification the individual particles cannot be resolved by ordinary light, and therefore, they should be of the order of 1 μ, or less. Again, I would point to the work of Sir Charles Goodeve on carbon-black suspensions, who showed that with a few

* *Rec. Trav. Chim. Pays Bas* (*Knuyt number*), 1946, **65**, 549.

consecutive milling operations one reaches an equilibrium with respect to thixotropy, and therefore probably with respect to the degree of dispersion. Thus I would point out that, by using a simple device, one can achieve the same degree of dispersion as by means of supersonic apparatus.

A particular feature of lubricating oils about which we have not heard this evening is that of acidity. In our laboratory we have observed some curious phenomena when acid is added to carbon-black suspensions. We use acid as an analytical device, not as a test of suspensions from the point of view taken in the paper.

Fig. 11 shows what happens if acetic acid or oleic acid is added to a carbon-black suspension which was originally so fine that the particles could not be resolved in the ordinary microscope. The carbon-black particles arrange themselves in chains. Normally, before the addition of acid, the particles or agglomerates cannot be distinguished at all.

I should like to ask what is the opinion of the authors on this matter, because the acidity of lubricating oils may be a factor in precipitating lacquer and other matter in engines.

Another matter I should like to raise deals with some previous work mentioned in the paper. Some workers report a decrease in the sedimentation volume with increase of polarity of the liquid. We find, however, that water, which is certainly the prototype of a polar liquid, increases the sedimentation volume. Without trying to put forward a new theory, I suggest that we might deal with the description of minute traces of water from various pigments on the addition of polar solvents. It is very difficult to prove anything of that kind, but I think it is a factor which should be considered, and I wonder whether the authors have gone to the trouble of determining the water content of their carbon black. We know they have dried their carbon black; but have they determined the water content at any stage?

Dr J. B. Matthews: I should like to raise a few points on the theoretical side of the work discussed in the paper. First, I would deal with the relationship between sedimentation volume and rate of sedimentation. My impression may not be correct, but I have interpreted the literature as indicating that the relationship is the reverse of that claimed by the authors. Thus, if we consider a dispersion in which flocculation has occurred, we obtain, as shown in Fig. 11, chains of particles forming flocs, and their rate of sedimentation will be greater than that of the primary particles. On the other hand, when we deal with the sedimentation volume, *i.e.*, the final volume of the sediment and not the volume of the dispersion during the course of sedimentation, if the dispersion is flocculated there is built up a rather loose type of structure having a bridge-work of these chains, so that the volume is greater than is the close-packed volume of the particles. In a completely dispersed suspension the particles exhibit no mutual attraction, so that when they do sediment they can slip past each other and form a closely packed structure. Thus, in a completely dispersed suspension, the sedimentation volume is smaller than in a flocculated suspension. If you accept this view, you will find that there is no incompatibility in the results quoted by the authors from Harkins and Gans, and Damerell and Urbanic. Thus, the former found that a surface-active material, *e.g.*, oleic acid,

decreased the sedimentation volume, and the latter found that surface-active agents decreased the rate of sedimentation.

The second point is the possibility of electrical charges operating in suspensions of carbon in non-polar liquids such as toluene. Theoretically, it is very difficult to visualize these electrical charges, and contradictory reports have been given in the literature concerning their existence. The authors quote McBain as stating that the type of surface-tension curve often obtained can be interpreted as an indication that an electrical charge of the Helmholtz type is involved. A few years ago, however, I showed that this type of curve is not necessarily valid, and may be only the result of wrong methods of measurement. In addition, Reichenberg has showed recently on theoretical grounds that the observed minimum in the curve may be only due to traces of impurities. Hence it is not necessary to postulate an electrical charge in order to account for the minima which sometimes occur in surface-tension curves. Apart from this, nevertheless, the authors state that they have observed a negative charge on the particles. I would ask them to say how this was measured, for this is a very important aspect of the matter.

Thirdly, the question of interpreting rates of sedimentation in terms of particle size is based on Stokes' Law, which really only applies to dilute suspensions in which no particle–particle interaction occurs. The suspensions described by the authors are fairly concentrated, however, and my colleagues and I have investigated still more concentrated suspensions, and, like the authors, have observed that a very sharp and clear boundary can be obtained. Theoretically, we should only get a sharp boundary if the particles are all of the same size, but in the case of the carbon used by the authors it is unlikely that the particles are all of the same size. In our own work we have found that the conditions of settling are not those to which Stokes' Law strictly applies. We must therefore conclude that there is some very complicated phenomenon occurring during the sedimentation of these suspensions which rather invalidates any conclusions upon particle size derived from rates of sedimentation. In this connexion, we have carried out extensive measurements on the size distribution of particles in used oils, and the results indicate that the particles in used engine lubricating oils are all of pretty well the same size. Thus, if it is intended to investigate the colloidal properties of used engine oils by studying synthetic dispersions, it may, perhaps, be desirable to choose suspensions in which the particles are uniformly sized.

Mr J. S. Elliott : I should like to ask whether the authors have any experience of the test known as the chromatographic detergency test.* Although we realize that it has many imperfections, it does seem to be on the same general lines as the method indicated by the authors.

Briefly, it consists in dispersing carbon black in the oil which is under test, drawing it through a column of sand or some substitute and determining the degree of penetration of the carbon black. We have tested quite a number of different metallic soaps with this apparatus, and although there are freak results, repeatability is in the main reasonably good, and a number

* Talley, S.K., and Larsen, R. G. *Indust. Engng Chem. Anal.*, 1943, **15**, 91–5.

of additives which are generally recognized as being of detergent type give quite good results. Others, which have little value as detergents, give poor results. The naphthenates, we have found, do not give such good penetration as the corresponding metal soaps of acids with long, straight chains.

One other point concerns the effect of water. The authors stress the necessity for controlling strictly the amount of water present, and to make their results reproducible they have a standard method of drawing moist air through the column before the test begins.

DR F. J. BURGER: Is it really necessary to assume that free electric charges are responsible for the forces of interaction between particles suspended in hydrocarbons? Attraction can be readily understood in terms of dipole and van der Waals' forces. As regards repulsion, I suggest that the action of certain detergents in keeping particles in stable suspension might be due to the active Brownian movement of the non-polar ends of the detergent molecules, their other ends being firmly attached to the carbon particles by virtue of a dipole moment or of van der Waals' forces.

MR J. C. MCNICOL: I was interested in the analytical method used, since it appeared that the authors had chosen to measure the small decrease in concentration of calcium napthenate in the liquid, by measuring the total concentration before and after the adsorption by the carbon. Would it not be simpler and more accurate to measure directly the amount of calcium naphthenate adsorbed on the carbon?

As a second point I would refer to Table II. I wonder whether the authors would explain the decrease in the $\frac{x}{m}$ ratio.

DR R. P. TAYLOR: Further to the remarks of Mr McNicol, with increasing concentration of calcium naphthenate, the degree of dispersion has increased. This improvement in the degree of dispersion corresponds with the adsorption of naphthenate on the carbon black. The optimum concentration of the calcium naphthenate is in the neighbourhood of 0·2 per cent, and this holds over a 10-fold change in carbon-black concentration. Would we not expect that this optimum concentration would be proportional to the carbon-black concentration? Furthermore, I think the data in Table I does indicate to a certain extent, that this is so. Would the authors care to comment further on this point?

MR E. THORNTON: At the end of the section of the paper dealing with the determination of the rate of settling, we are told that the progress of settling could be followed by the sharpness of the upper surface of the carbon suspensions. I was wondering on what evidence the statement is made that the finer particles settle more slowly. One would certainly expect this, but it is not clear whether it has been demonstrated, or this is an assumption.

If, however, it is so, surely the fall of the upper boundary line will measure the rate of settling of the finest and most laggard particles, rather than the average rate, as inferred in the paper.

A second point: were any repeat settlings carried out on once-settled suspensions?

If the equilibrium concentration and full and final adsorption were complete before the first settling took place, one would expect no change after re-dispersing and re-settling, but I see nothing to indicate whether any attempt was made to find out whether full adsorption and equilibrium concentration were really attained before the first settling.

Another point, does the supersonic method of dispersion make, in affect, a new kind of material from the original carbon black by altering its state of aggregation, and does the process end with one dispersion?

With regard to the comparison of the adsorptive capacity of various carbon blacks, I wonder if these blacks were tested after supersonic dispersion and whether the figures obtained might be different if other methods of dispersion had been used.

With regard to carbon black itself, the makers of channel black claim to have shown by electron-microscope measurements that their blacks differ from furnace blacks. They also claim activity for their channel black on account of residual chemical affinity. Was any account taken of this in deciding to use carbon black or the possibility that such properties might affect the absorption characteristics, or might confer absorption characteristics not possessed by the inert products of decomposition formed in engine oils?

DR J. TADAYON: The authors state that in analysing for calcium naphthenate, after final sedimentation volume was recorded, a sample of the clear solution above the suspension boundary was withdrawn for analysis on the Langmuir trough. It has been previously shown by the authors that calcium naphthenate was formed as a monolayer of the liquid-expanded type on the surface of the water. It is possible that at this stage of sedimentation some carbon suspension may still be present in the sample. These may impose a new orientation in the film affecting its normal structure, and consequently the method may not give a high degree of accuracy.

THE AUTHORS in reply to the discussion stated that they shared the President's idiosyncracy as regards to use of the word " carbon " to describe certain types of engine deposits; the presence of oxygen compounds is mentioned in the paper. His criticisms of the use of the word carbon are similar to those he made on a paper by one of the authors presented before the Institution in 1921 (*J. Inst. Petrol. Techn.*, 1921, **7**, 98), so in that he is at least consistent.

It was interesting to have the contribution from M. Roegiers, who has a detergent additive which has the advantage that it is free from the presence of metallic compound. We were also pleased that Dr Van de Minne drew attention to the somewhat contradictory effects of oil resins and particular additives as regards detergency.

As regards the method of dispersion mentioned by Mr Grunberg, we have heard of pestles and mortars. We rejected their use early in our work because we did not wish to reduce the carbon black to smaller dimensions by attrition. Referring to the acidic components of used oil, these are likely to be present in the resins which are probably of a relatively high

molecular weight, and hence may have a peptizing effect rather than one of flocculation. Water plays quite a different part in precipitation from other polar liquids, and it is wrong to use the terms polar and non-polar liquids as though they were mutually exclusive and completely explanatory. The carbon black which we used was dried at a high vacuum and at a raised temperature, and we have not attempted to determine its moisture content, as we know of no suitable method.

Dr J. B. Matthews referred to the photograph shown by Mr Grunberg of a carbon-black suspension to which acetic or oleic acid was added; the carbon-black particles were arranged in chains, and thus exhibit flocculation as described by Dr Matthews. Such a structure if formed with such relatively inert solvents as benzene, would lead to large sedimentation volumes and at the same time show a relatively slow rate of sedimentation. It is rather difficult to explain how low sedimentation volumes (in which this supposed bridgework of chains is presumably not present) can also be found with slow rates of sedimentation of particles containing adsorbed material. It is for this reason that electrical charges may well be the explanation, and this does not depend on the truth or otherwise of the minimum of the surface-tension curves found by McBain. The presence of additives on carbon black leads to an effect similar to that of jelly in frog-spawn, in that the carbon-black particles are held up and apart from each other in the liquid medium.

We know that the adsorbed layer of additive on the carbon black is not likely to be more than one or two molecules thick, but that it will have the effect of orienting the surrounding solvent and solute molecules. Such orientation will set up a potential barrier between the particle surface and the bulk liquid, so that before contact and cohesion of two adjacent particles can take place work must be performed against this energy barrier.

Such a barrier will be absent where there is no adsorbed layer, and so less energy will be required to bring about cohesion.

Stokes' Law applies only in the case of fairly dilute suspensions, but does give a general picture of the settling which takes place in more dense suspensions, and smaller particles will settle at a slower rate than larger ones, assuming other conditions are equal. However, in a suspension where the range of particle sizes is not too great and the volume concentration of solids is above about 1 per cent, once settling begins the larger particles falling more rapidly will leave the smaller particles settling in a much more dilute suspension. Thus, under certain conditions the retardation experienced by the larger particles as a result of their being present in a more concentrated suspension will be sufficient to neutralize the greater velocity which they derive from their larger size, so that the finer particles will catch up with the larger ones, and the result will be a sharp boundary between the particles and the liquid medium above. This seems to us to provide the most probable explanation of this sharp boundary. The particle charge on the blacks was detected by watching the fall of particles in toluene between two electrodes and observing their motion when a p.d. of 500 V was applied in each direction. Precautions were taken to ensure that no charge was acquired by contact.

We were particularly interested in Dr Matthews' observations that the

carbon particles in used engine lubricating oils are all of much the same size. We should have liked to have had some information of the method used to prepare the carbon particles for examination free from oil and other adsorbed material, since carbon particles agglomerate relatively easily under suitable conditions, as, for example, sludges present in the crankcase, and may be present in the used oils in a variety of sizes.

In reference to the chromatographic detergency test referred to by Mr J. S. Elliott, we feel that this method introduces a factor which is not necessarily related to detergency, namely the influence of the surfaces present on the adsorbent or filter. In our investigation, it was felt to be essential to compare settling rates (as a measure of detergency or dispersivity) with the mechanism of adsorption of additive on the carbon black. The paper referred to by Mr Elliott shows important discrepancies between different methods of test which have not so far been explained.

In reference to the comment made by Dr Burger, it is difficult to see how repulsion can be explained by Brownian movement of the unipolar end of the molecules, since Brownian movement is due to the bombardment by molecules in the liquid and should have no effect on adjacent particles.

As Mr McNicol points out, it would have been preferable to determine the percentage adsorption on the carbon black, but we could think of no suitable method. As regards the decrease in $\frac{x}{m}$ ratio shown in Table II, since an equilibrium must exist between the calcium naphthenate adsorbed and that in solution, it is logical to expect the $\frac{x}{m}$ ratio to decrease with increasing concentration of carbon black. An extension of this point has been mentioned by Dr Taylor, and we agree that the optimum concentration would be expected to vary with the carbon-black concentration, and as Dr Taylor points out, this is borne out to some extent by the data in Table I, but is a point which had not previously occurred to us.

In reply to Dr Tadayon, we would expect that if particles were present in the size range below, but of the order of 1 μ, they would exhibit some light-scattering effect in suspension, but this could not be detected—so that their concentration, if any are present, could have but slight effect on molecular orientation in a monolayer.

Some of the points raised by Mr Thornton have been already discussed; no repeat settlings were made on once-settled carbon suspensions. The main point of the supersonic method of dispersion was to break up the carbon-black aggregates as far as possible into the component particles, but this was not wholly achieved. There is no doubt that different carbon blacks would have different adsorptive capacity, and we would refer Mr Thornton to a recent paper,* which gives an account of the adsorption of a number of fatty acids on carbon blacks of different types.

It is an essential academic requirement that as pure materials as possible should be used, and this scientific requirement is of the utmost practical importance, since traces of impurities will influence the results to a marked extent. Therefore the only practical plan is to take pure materials and add traces of impurities to determine the effect of the second component. The

* *Industr. Engng Chem.*, 1948, **40**, 2325.

use of impure materials *may* lead to the rapid development of commercial additives or may lead to complete failure.

Vote of Thanks.

The President: We are deeply indebted to Mr Baddeley, Dr Nissan, and Professor Garner for their paper on this very beautiful work.

Professor Garner was a little amused by my opening comment with regard to the mind in an academic environment; I did not say "the academic mind", for that is not quite the same thing. But we do like to know that this very beautiful work is going on in the universities, work which I think it would be very difficult indeed to put into operation in ordinary commercial laboratories. This system of segregating the parts of a problem into their proper compartments is really the only way in which to deal with a complex subject such as that which we are handling this evening.

I cannot help feeling that perhaps those who are working in the academic field are so pure that they are apt to overlook some of the "impurity" of the technical mind. I am not speaking of that from the moral aspect; far be it from me to deal with that. I can only look at it from the very practical aspect; and if we in the commercial field had investigated the additives as pure substances we should have missed the whole objective. I am perfectly certain that a good many people would have found really good additives if they had worked with materials which are a little less pure. For example, the ordinary hypoid lubricant is almost useless when perfectly pure; there must be impurity. Practically all the additives which are in use successfully are contaminated with some impurity, or alternatively, their activity is brought out only when there is a second material present. That is by no means intended to be a humorous remark; the matter is all too serious. A paper from Cambridge was published in our *Journal* quite recently, the authors may not have appreciated this point.

My duty now is, on your behalf, to thank the authors of the paper for the great work they are doing and for the simple way in which they have explained this very deep subject to us. I think the discussion has proved that they are dealing with a subject of real scientific importance. I ask you all to join with me in thanking them very much indeed.

(The vote of thanks was accorded with acclamation; and the meeting closed.)

REACTION OF SULPHUR, HYDROGEN SULPHIDE, AND MERCAPTANS WITH UNSATURATED HYDROCARBONS.*

LITERATURE SURVEY.

By W. H. Hoffert (Fellow), and K. Wendtner.

Introduction.

The reactions of sulphur and sulphur compounds are of considerable importance in connexion with the recovery and refining of benzoles. Although the thickening and sludging of wash oils appears to be basically an oxidation process, the deterioration of these oils is accelerated when both hydrogen sulphide and oxygen are present. Moreover, there is an accumulation of sulphur in the oxidation or condensation products responsible for the thickening and sludging, indicating that hydrogen sulphide must have played some part in the reactions involved.[1] Again, it is known that benzole recovered from unpurified gas can be refined more easily if the crude benzole is washed free from hydrogen sulphide immediately after the benzole is stripped from the oil, and before the hydrogen sulphide has time to oxidize to elementary sulphur, or react directly with constituents of the benzole. During the final distillation, there is sometimes a reversal of these reactions, and hydrogen sulphide and mercaptans are formed. Knowledge, therefore, of the conditions under which sulphur and sulphur compounds react with unsaturated hydrocarbons, and of the mechanism of these reactions, should enable improvements to be made of both the benzole-recovery and refining processes.

Formation of Sulphur-containing Sludge from Wash Oils Used for Benzole Recovery.

The thickening and sludging of wash oils have been ascribed by a number of investigators to reaction of hydrogen sulphide in the gas with unsaturated hydrocarbons, derived from the gas, or present in the fresh oil, or produced by thermal decomposition of constituents of the oil.

Whitehead reported in 1920 that hydrogen sulphide apparently combines with certain constituents of paraffinoid wash oils to form complex sulphur

* In the earlier literature there is much confusion in the nomenclature of the olefins. Rules known as the Geneva System have now been agreed for the names of these hydrocarbons and other organic compounds. According to these rules, compounds containing the –SH group should be called thiols, and those containing the –S– and $-S_2-$ groups, etc., thio, dithio, etc. ("Definitive Report of the Commission on the Reform of Nomenclature of Organic Chemistry," International Union of Chemistry, 1930; *J. Chem. Soc.*, 1931, 1610; 1936, 1067). In this survey however, owing to doubt concerning the exact constitution of some olefins reported in the literature, the names used by the authors have generally been retained, and the older and more familiar names of mercaptans, sulphides (thioethers), and disulphides have been used for compounds containing the –SH, –S–, and $-S_2-$ groups. For the properties of organic sulphur compounds, see U.S. Bureau of Mines Report of Investigations 4060, Dec. 1946.

compounds, probably mercaptans. These compounds decompose at about 140° C, and on distillation in the laboratory large volumes of hydrogen sulphide are evolved at about this temperature. Whitehead attributed serious corrosion of pre-heaters to this effect, and pointed out that the presence of ammonia in the gas appeared to be necessary for the reaction to proceed. When corrosion occurred a trace of ammonia was present, whereas the washing of ammonia-free gas with similar oil often continued without trouble.[2] Similarly, Offe concluded that the thickening of coal-tar oils was due to reaction between hydrogen sulphide and unsaturated constituents of the oil to form a compound that decomposed above 210° C with the evolution of hydrogen sulphide and separation of carbon.[3] Kattwinkel attributed the thickening of coal-tar oils to sulphuric acid and sulphur,[4] and Bordo and Mühlendyck to sulphur formed by oxidation of the hydrogen sulphide.[5] According to Demann and Brösse, a series of reactions occurs as follows. Hydrogen sulphide is absorbed by the oil at atmospheric temperature with the formation of an additive compound, a reaction that is reversible under certain conditions. Oxygen then reacts with the additive compound at higher temperatures to give elementary sulphur, which at temperatures above 120° C reacts with the tar-oil constituents, forming organic sulphur compounds and hydrogen sulphide.[6] Recently, Kattwinkel has modified his earlier views, and from an examination of the "asphalt" and "pitch" from thickened wash oils has concluded that the thickening is due to condensation and polymerization processes involving interaction of mercaptans, disulphides, and heterocyclic sulphur compounds formed by the action of hydrogen sulphide on unsaturated compounds in the oil. During preheating, these sulphur compounds split up, the disulphides probably with the intermediate formation of sulphides into hydrogen sulphide and elementary sulphur, which condenses wash-oil constituents to substances of high molecular weight. If oxygen is present, mercaptans are oxidized to disulphides, and sulphonic and sulphuric acids are formed by hydrolysis of –SS– compounds, these reactions, however, being of only a secondary nature. Oil regenerated by precipitation of the "asphalt" with solvents still contains the active sulphur compounds and is less stable than fresh oil. The active sulphur compounds can be removed by redistilling the oil.[7] Oppelt and Münz found that oxygen alone caused the rapid formation of "asphalt" from creosote, whereas hydrogen sulphide alone caused only slow thickening. When both were present, however, "asphalt" formation was accelerated.[8] Kolkenbrock[9] is reported by Jenkner[10] to have found that ammonia and hydrogen sulphide had a thickening action on creosote, but ammonia alone was without effect. Ashmore has attributed the formation of sulphur-containing sludge to reaction between elementary sulphur and unsaturated compounds, such as indene, in the wash oils. Elementary sulphur, presumably formed by oxidation of hydrogen sulphide, was found to be present in amounts varying from 0·01 to 0·60 per cent w/v in wash oils used for scrubbing unpurified gas. This sulphur reacts above 150° C with indene and other unsaturated compounds to form di-indenethiophen and similar thiophenic compounds. Both the elementary sulphur and the thiophenic compounds react with more of the unsaturated compounds under the influence of heat to form first soluble sludge, which is then converted into insoluble sludge, either by

reacting with more of the unsaturated compound, or by direct polymerization.[11]

That some investigators have attributed a primary rôle to hydrogen sulphide in the deterioration of wash oils has been mainly due to the high amounts of sulphur in the material responsible for the thickening and sludging. Offe found that the solid material separated from the pitchy deposit obtained by adding paraffin oil, gas oil, or benzene, to a used wash oil had the following composition : C = 74·4 per cent, H = 5·4 per cent, S = 6·46 per cent, N = 1·82 per cent, and O = 11·92 per cent w/w.[12] Kattwinkel found that the " wash-oil asphalt " separated from a used wash oil by dissolving it in chloroform and then adding excess of light petroleum, and the " wash-oil pitch " obtained by precipitation of the wash oil with benzene, contained 11·2 and 10·2 per cent w/w of sulphur respectively.[13] Oppelt and Münz found that the " asphalt " obtained from a used coal-tar oil by dissolving the oil in benzene and precipitating the asphalt with light petroleum contained 5·10 per cent w/w of sulphur, compared with 2·0 per cent in the oil itself, and 0·77 per cent in the fresh oil.[8] From 1·0 to 14·3 per cent w/w of sulphur was found by Dick, Claxton, and Hoffert in the oil- and water-free deposits from plants using petroleum oils. The sulphur and the oxygen were highest in the sludges that had been subjected to heat.[14]

Formation of Sulphur, Hydrogen Sulphide, and Mercaptans during the Refining of Benzoles.

The removal of hydrogen sulphide from crude benzole directly after production by washing with caustic-soda solution of 18 per cent strength has been patented by Carl Still.[15] The object, according to the patent, is to remove the hydrogen sulphide before atmospheric oxidation can occur with the formation of elementary sulphur or of sulphur compounds that are not susceptible to removal by the usual refining methods. Attention has been drawn by various investigators to the importance of carrying out this preliminary alkali wash as early as possible.[16] Kiemstedt considers this necessary so that the hydrogen sulphide does not oxidize or react with constituents of the benzole.[17]

There are further reasons for the removal of hydrogen sulphide as the first operation in the refining of crude benzole. Concentrated sulphuric acid oxidizes hydrogen sulphide to elementary sulphur and mercaptans to disulphides :—

$$RSH + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 \longrightarrow \begin{matrix} RS \\ HO \end{matrix}\!\!>\!SO_2 + H_2O \xrightarrow{(RSH)} \begin{matrix} RS \\ RS \end{matrix}\!\!>\!SO_2 \longrightarrow \begin{matrix} RS \\ RS \end{matrix}\!\!>\!+ SO_2,$$

the intermediate products, thioalkyl acid and di-thiosulphate, being formed when the quantity of sulphuric acid is insufficient to oxidize the mercaptan completely to disulphide.[18] The elementary sulphur can then combine with the disulphides to form corrosive polysulphides, the reactions being represented by the following equations :—

$$2RSH + O = R_2S_2 + H_2O$$
$$2RSH + S = R_2S_2 + H_2S$$
$$R_2S_2 + S = R_2S_3$$[19]

Less concentrated acid causes a reaction between hydrogen sulphide and unsaturated hydrocarbons, producing mercaptans.[20] At the present time, many refiners are using a continuous alkali-washer on the freshly condensed benzole from the stripping-still with beneficial results.

Hydrogen sulphide and mercaptans are sometimes produced towards the end of the final distillation and reappear in the refined benzole. These compounds may result either from the action of elementary sulphur on mercaptans and hydrocarbons respectively, or from the thermal decomposition of certain sulphur compounds.

In addition to the corrosive character of elementary sulphur and the objectionable odour of mercaptans, the latter have been reported to cause colour instability on exposure to light. Egloff, Morrell, Benedict, and Wirth found that elementary sulphur, and to a less extent disulphides and mercaptans, caused the deterioration in colour under these conditions of straight-run and cracked gasolines.[21] These effects were confirmed by experiments with various pure hydrocarbons. Except for benzene, colour and haze formed only in the presence of sulphur and of *n*-propyl disulphide on exposure to light in oxygen, nitrogen, or hydrogen. In oxygen, peroxides, aldehydes, and acids were formed. In nitrogen and hydrogen, reaction of sulphur with saturated hydrocarbons occurred, resulting in colour formation and evolution of hydrogen sulphide. Unsaturated hydrocarbons, similarly exposed, produced coloured compounds, hydrogen sulphide, and mercaptans.[22]

Mercaptans also take part in gum formation. Hoffert and Claxton, in their investigations on the use of inhibitors for preventing gum formation, found that when ethyl mercaptan or thiophenol was added to unstable benzoles, the quantity of gum formed in the N.B.A. oxidation test (3 hr) was considerably increased. The additional amount of gum formed, which increased with increase in the quantity of added mercaptan, varied from nine to three times the amount of mercaptan added. When cresol was added in increasing amounts to a benzole containing thiophenol, the amount of gum formed could not be reduced below about 50 mg per 100 ml of benzole, whereas in the absence of the thiophenol the gum was reduced to a few milligrams (with 0·05 per cent w/w of cresol). The curves for the reduction in gum formation on the addition of increasing amounts of cresol in the absence and presence of a fixed amount of thiophenol were roughly parallel.[23] Although it was concluded, at the time, that mercaptans are accelerators of gum formation, a considerable proportion of the increased gum formed in the presence of mercaptan was probably due to combination of the thiophenol with some of the unsaturated hydrocarbons to give non-volatile compounds of high molecular weight.

Kruber and Schade, after removing di*cyclo*pentadiene from benzole forerunnings, found that on fractionation sulphur compounds were contained in increasing amounts in the higher-boiling fractions and in the distillation residue. Ethyl mercaptan was obtained by depolymerization of the residue. They were able to prepare addition compounds of ethyl mercaptan and *cyclo*pentadiene, *cyclo*hexene, styrene, 1 : 2-dihydronaphthalene, and di*cyclo*pentadiene, and concluded that mercaptans add to unsaturated compounds on storage to give non-volatile material.[24]

Sulphur compounds, particularly disulphides and mercaptans, also have a deleterious effect on the lead response of motor fuels.[25]

In the literature survey given below of the reactions of sulphur, hydrogen sulphide, and mercaptans with unsaturated hydrocarbons, attention has been paid mainly to the temperatures and other conditions under which reaction has been reported and to the products of reaction.

Action of Sulphur on Unsaturated and other Hydrocarbons.

The reaction of sulphur with various aromatic, saturated, and unsaturated hydrocarbons is reported in the literature.

Ethylene, Acetylene.

Victor Meyer found that when either ethylene or acetylene is passed through boiling sulphur, hydrogen sulphide, carbon disulphide, and thiophen are formed.[26] The same products were obtained by Peel and Robinson, as well as a substance with a garlic-like odour, when acetylene was passed through sulphur below its boiling point. At 325° C, 38 per cent of the sulphur was converted into a brown oil, which had the composition : 77 per cent carbon disulphide, 9 per cent thiophen, and 6 per cent thiophtene.[27a] The thiophen was shown by Briscoe, Peel, and Robinson to be formed by direct reaction with sulphur, and not by a secondary reaction with carbon disulphide.[27b] Bhatt, Nargund, Kanga, and Shah identified thiophenol in the reaction products obtained on heating acetylene and sulphur at 290° to 390° C, thus accounting for the garlic-like odour observed by Peel and Robinson.[28] Challenger and Harrison found that not only thiophen, but the isomeric thiophthens were formed when acetylene was passed through the vapour of boiling sulphur.[29] According to Hessle, thiophen derivatives are formed at lower temperatures (200° to 250° C) if cracked distillates are substituted for acetylene.[30] Meyer and Hohenemser found that there was no reaction between sulphur and ethylene at 150° C.[31] Jones and Reid passed ethylene through sulphur at 325° C and obtained much hydrogen sulphide, 3 per cent of ethyl mercaptan, and small amounts of ethyl sulphide and carbon disulphide.[32] The mercaptan and sulphide were formed apparently by side reactions between the ethylene and the hydrogen sulphide, and of more ethylene with the mercaptan. By reacting ethylene with sulphur under pressure at temperatures of 124° to 145° C, using xylene as a solvent, Westlake, Mayberry, Whitlock, West, and Haddad obtained an insoluble elastomer and a xylene-soluble oil as the main products.[33]

Higher Olefins.

Friedmann heated hexene, octene, and hexadecene with sulphur under pressure at 270° to 280° C. From hexene he obtained a mixture of sulphur compounds of the composition $C_6H_{12}S$, $C_{12}H_{24}S$, and $C_{18}H_{34}S$, as well as an asphaltic non-volatile residue of the composition $C_{24}H_{20}S_2$. Similar products were obtained from octene ($C_8H_{12}S$ and $C_{16}H_{28}S$) and from hexadecene ($C_{16}H_{32}S$). He concluded that the reaction gave first hydrogen sulphide, which added to the double bond to form a thioglycol. Hydrogen sulphide then split off with the α-methylene to give an unsaturated mercaptan.[34] Armstrong, Little, and Doak, by reacting a number of higher olefins with sulphur at temperatures of 120° to 140° C and both with and without

catalysts (rubber accelerators), obtained volatile and non-volatile products in varying amounts, depending on the olefin and the conditions. 2-Butene formed crotyl mono- and di-sulphides together with polymerized material. 2-Methyl-2-butene and 2-methyl-1-butene gave mixtures of the mono- and di-sulphides of allylic radicals both symmetrical and unsymmetrical, as well as polymer. Similar products were obtained from 5-methyl-4-nonene. The amount of hydrogen sulphide evolved from this olefin when heated with sulphur in a stream of nitrogen at this temperature amounted to much less than 1 per cent of the sulphur combined. They concluded that at moderate temperatures, sulphur combines with olefins without degradation or elimination of hydrogen sulphides, and establishes " cross-links," consisting apparently of polysulphides, between the mono-olefin molecules.[35]

cyclo-*Olefins.*

In a study of the constitution of naphthenes by dehydrogenation with sulphur at 210° to 220° C (Vesterburg reaction), Markownikoff and Spady observed the formation of high-boiling sulphur compounds in addition to benzene and its homologues.[36] Friedmann showed that the dehydrogenation of *cyclo*hexane with sulphur under pressure at 250° to 260° C for 24 hr gave thiophenol, phenyl sulphide, and polysulphides.[34c] Meyer and Hohenemser found that when *cyclo*hexene was heated with sulphur at 150° C about two-thirds reacted with both sulphurization and reduction to form *cyclo*hexyl mercaptan, di*cyclo*hexyl sulphide, and a residue of sulphurized oils of high boiling point.[31] Armstrong, Little, and Doak obtained at a somewhat lower temperature (136° C) only non-volatile polysulphides $(C_6H_{10}S_4)_x$, where $x = 3{\cdot}5$. No mercaptan or sulphide could be detected.[35]

Styrene and Diolefins.

A few investigations of the reaction of sulphur with *cyclo*pentadiene, styrene, and indene, the chief unsaturated hydrocarbons in benzoles, have also been reported.

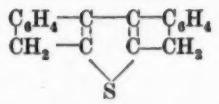
Mayberry, Westlake, and Fanelli found that sulphur reacts with *cyclo*pentadiene at about 120° C to form products that at first were slightly elastic, but became hard and brittle on standing.[37] Deposits of this nature have been reported on wash oils used for benzole recovery.

By reacting styrene (or cinnamic acid) with sulphur at 210° to 225° C for several hours followed by refluxing for 6 hr at 230° C, Baumann and Fromm obtained a mixture of diphenylthiophenes.[38] Michael reported the isolation of a compound having the composition C_8H_8S by heating styrene for 12 hr at 150° to 160° C,[39] whereas Meyer and Hohenemser obtained only 2 : 4-diphenylthiophen at 150° C.[31] Westlake sulphurized styrene in xylene solution * and obtained as the sole product a mixture of the average composition $(C_8H_8S_3)_{2{\cdot}5}$, which could be decomposed by pyrolysis to diphenylthiophen.[40]

Friedmann heated indene with sulphur in the proportions 100 parts of indene to 28 or 56 parts of sulphur at a temperature of 180° to 185° C and obtained various products containing 6·7 to 17·0 per cent w/w of sulphur.

* Temperature not stated, but presumably 124° to 145° C, cf. ref. 35.

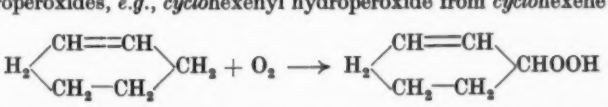
The simplest, which was fairly soluble in toluene and had the empirical formula $C_{18}H_{12}S$, he concluded was di-indenethiophen :—



Other less-soluble products had the empirical formulæ $C_{36}H_{24}S$, $C_{36}H_{22}S$, and $C_{36}H_{24}S_3$. At the highest temperature, the products were similar to asphalt.[34]

By heating butadiene and sulphur at about 350° C, Shephard, Henne, and Midgley obtained a 6 per cent conversion to thiophen, while isoprene gave a 47 per cent conversion to 3-methylthiophen under these conditions.[41] Westlake found that butadiene was readily sulphurized by heating * under pressure in xylene solution to give red odorous oils resembling ethylene sulphides.[40]

These results indicate that the higher olefins and diolefins are sulphurized more readily than the gaseous olefins, and support the conclusion that the first reaction is the addition of sulphur to the double bond rather than elimination of hydrogen sulphide and its immediate addition to the double bond under the catalytic influence of the sulphur. Farmer and his co-workers, however, have evolved a theory, based on their own and other researches on oxidation, according to which the α-methylene group is first attacked, and not the double bond, with the formation of either unsaturated mercaptans or unsaturated sulphides in a similar manner to the formation of hydroperoxides, *e.g.*, *cyclo*hexenyl hydroperoxide from *cyclo*hexene [42] :—



The evidence for and against this theory has been discussed by Westlake in a review of the sulphurization of unsaturated compounds and the vulcanization of rubber.[40]

More recently, Farmer and Shipley, continuing their investigation on the mechanism of the vulcanization of rubber have shown that reaction of sulphur with olefinic materials is usually appreciable at 100° C and proceeds at a moderate rate of 140° C, the temperature used in their experiments. Sulphurized products, which were sensitive to elevated temperature and necessitated separation by molecular distillation, were obtained, and were identified by infra-red analysis as a series of polysulphides RS_nR', where n is 1 to 4. These polysulphides at higher temperatures gave alkyl mercaptans, dialkyl sulphides, and hydrogen sulphide, which therefore are only secondary products of the olefin–sulphur reaction.[43] The existence of polysulphides, RS_nR where $n = 3$, 4, or 5, containing three sulphur atoms in a linear arrangement and having no analogues amongst oxygen compounds, had been reported previously by Claesson,[44] Smythe and Forster,[45] and other investigators. Organic monosulphides do not react readily with sulphur or metal polysulphide, but the disulphides react at 150° C.[44] Under similar conditions, trisulphides and tetrasulphides are converted into

pentasulphides, the reaction apparently being catalysed by ammonia.[46] The lower sulphides are obtained from the higher sulphides by reversing these reactions by distillation.[47]

Various condensation products of sulphur and olefinic compounds have been patented. For example, B.P. 530,026 describes the production of sulphur-containing condensation products by heating sulphur with olefinic hydrocarbons, such as ethylene and indene, or tar-oil fractions containing indene, at 100° to 120° C.[48] According to U.S.P. 2,337,473, hydrocarbon mixtures containing unsaturated compounds are sulphurized by treatment with sulphur at temperatures of 150° to 190° C in the presence of hydrogen sulphide at a pressure of 50 p.s.i.[49] U.S.P. 2,402,643 describes the production of mercaptans by hydrogenating sulphurized products obtained by heating unsaturated compounds, *e.g.*, styrene, with benzene and sulphur at 160° C.[50] Polymeric linear polysulphides (thiokols) prepared by the reaction of dihalides with sodium tetrasulphide have been used in place of natural rubber, when resistance to petrol and other solvents is important.[47] The combination of olefins and sulphur by submitting the hydrocarbon to the simultaneous action of sulphur and hydrogen sulphide is described in F.P. 787,810.[51] Basic substances, such as ammonia, amines, piperidine, etc., can be used as carriers for the sulphur. An example of their use is in the vulcanization of rubber.[52]

Sulphur has been reported to react also with aromatic hydrocarbons and with paraffins, but at higher temperatures. Aronstein and van Nierop found that sulphur reacted with toluene at 200° C to form stilbene and hydrogen sulphide.[53] Palmer, Lloyd, and their co-workers, by passing the vapours of benzene, toluene, and other organic substances through molten sulphur at 200° to 260° C obtained various resinous sulphur dyes, some of which were rubber-like after purification. Within the range 260° to 300° C non-resinous sulphur compounds that were not dyes resulted. More hydrogen sulphide was evolved as by-product in the reaction below 260° C, than in that above 260° C. Above 300° C, another class of sulphur dyes are formed.[54] By heating benzene with sulphur for 24 hr at 350° C, Glass and Reid obtained thiophenol, diphenyl sulphide, diphenyl disulphide, diphenylene disulphide, and hydrogen sulphide. The reaction with ethylbenzene at this temperature was quite different and much more rapid, an excellent yield of 2 : 4-diphenylthiophen being obtained.[55]

Friedmann found that *n*-heptane and *n*-octane reacted with sulphur when heated in an autoclave at 275° to 285° C to give branched-chain sulphur compounds. Branched-chain compounds, *e.g.*, *iso*octane, formed sulphides as well. The ring compounds react further to give thiophens, thiophthen, and thiophanes, etc.[34] Rasmussen, Hansford, and Sachanen found that when butane is bubbled through molten sulphur at 300° to 400° C no olefin is formed, but when butane and sulphur vapour are heated to 600° to 650° C, butene, butadiene ($CH_2 = CH_2)_2$, and thiophen are found, and this reaction has been used for the production of thiophen on the commercial scale.[56]

The greater reactivity of sulphur with unsaturated hydrocarbons than with other types of hydrocarbons has led to proposals for using this element as a refining agent. Bielenberg investigated the reaction of sulphur with a lignite-tar oil and found that evolution of hydrogen sulphide commenced

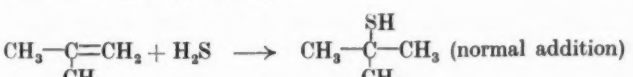
at 130° C. Fractions from the treated oil had higher sulphur contents and lower iodine numbers than the corresponding fractions of the original oil.[57] According to Kattwinkel,[58] in one of the early Stegemann processes benzole was treated with 1 per cent of sulphur, the bromine number being reduced by about 90 per cent leaving a marketable pitch with little material loss. A similar process was described by Uloth, who heated crude benzole with 1 to 2 per cent of sulphur under pressure. Reaction commenced at 110° C and was almost complete at 270° C. Pressure had little effect. The product was reported to contain only traces of elementary sulphur, and about half the combined sulphur to be contained in a small quantity of pitch that was formed.[59] This process, which is also described in B.P. 306,421 [60] and F.P. 710,723, in which heating to temperatures above 80° C is mentioned, is reported to be applicable to the regeneration of wash oils.[61] The use of 6 to 10 per cent of sulphur is claimed in U.S.P. 1,896,226 for refining cracked petroleum distillates.[62]

Action of Hydrogen Sulphide on Unsaturated Hydrocarbons.

The direct combination of hydrogen sulphide and olefins would be expected to proceed according to the general equation :—

$$C_nH_{2n} + H_2S = C_nH_{2n+1}SH$$

With unsymmetrical olefins, the formation of two isomeric mercaptans is possible, depending on the carbon atom to which the sulphur becomes attached. If Markownikoff's rule [63] is obeyed, the sulphur should appear on the carbon atom carrying the smaller number of hydrogen atoms, or the larger number of alkyl groups, *e.g.* :—



*Iso*Butene (methylpropene)

*Iso*Butyl mercaptan (*iso*methylpropyl thiol)

Vapour-phase Reaction under Pressure.

A survey of the literature shows that this reaction does not take place readily with the simple olefins, that fairly high temperatures and pressures are required, and that various catalysts for this reaction have been used.

The effect of temperature (200° to 300° C) and catalysts on the conversion of hydrogen sulphide and propylene to mercaptan was investigated by Duffey, Snow, and Keyes. They found that some catalysts promoted polymerization and decomposition. The best catalysts were nickel on kieselguhr, phosphoric acid, and bentonite. Maximum conversions ranged from 17 per cent at 200° C (space velocity 2 to 9) to 9 per cent at 300° C (s.v. 23).[64] This reaction was further studied by Barr and Keyes, who found that with a nickel-sulphide catalyst and temperatures of 200° to 300° C, *iso*- and *n*-propylmercaptans were formed approximately in the ratio of 2 : 1. The largest yields were obtained at the lowest temperature, as shown by the data in Table I selected from those given in their paper :—

TABLE I.

Temperature (°C).	Total conversion (%).	Mercaptan.	
		*iso*Propyl.	*n*-Propyl.
200	50	32·5	17·5
250	29	18·8	10·2
300	12	7·8	4·2

The equilibrium constant (K) between 200° and 300° C varied from 1·95 to 0·189 for the formation of the *iso*mercaptan, and from 1·05 to 0·102 for the formation of the *n*-mercaptan.[65]

Ipatieff and Friedman examined the addition of hydrogen sulphide to propylene, *iso*butylene (2-methylpropene), trimethylethylene (2-methylbutene-2), and *iso*propylethylene (3-methylbutene-1) in a stainless-steel vessel, but without added catalysts, and obtained the results shown in Table II :—

TABLE II.

Mol. H_2S.	Olefin.	Mol.	Time (hr).	Temp (°C).	Yield (%).	Products.
1·05	$CH_2{=}CH(CH_3)$	1·1	3	150	<1	Mixture
			4	200	4	"
1·3	$CH_2{=}C(CH_3)_2$	1·5	4	100	9	t-C_4H_9SH
			5	150	36	t-C_4H_9SH + 2t-$(C_4H_9)_2S$
1·5	$(CH_3)_2C{=}CH(CH_3)$	0·57	8	150	45	t-$C_5H_{11}SH$
0·66	$CH_2{=}CH{-}CH(CH_3)$	0·428	5	150	No mercaptan	

At higher temperatures side reactions occurred. They concluded that the hydrogen sulphide adds according to Markownikoff's rule, that the yield of product increases with increased branching of the olefin, and that excess of hydrogen sulphide favours the formation of mercaptans, whereas excess of olefin leads to the formation of thioethers.[66]

At high temperatures, cracking, cyclization, and condensation occur. Thus, Mailhe and Renaudie, using a silica-gel catalyst at temperatures of 650° to 725° C, found that condensation of ethylene, propylene, butene-1, and amylene to higher-boiling chain- and ring-hydrocarbons occurred, or decomposition into hydrogen and saturated and unsaturated hydrocarbons, which in turn reacted with hydrogen sulphide. Mercaptans decomposed into neutral sulphides, which gave thiophen and its homologues. Carbon disulphide was also formed in increasing amounts with increase in temperature.[67]

Jones and Reid found that the addition of hydrogen sulphide to unsaturated hydrocarbons took place readily when they were heated in a bomb at 180° C (10 hr) in the presence of elementary sulphur, which acted as a catalyst. In the absence of the sulphur there was little if any addition. The sulphur was found on the secondary and tertiary carbon atom in accordance with Markownikoff's rule (Table III). In all their experiments the mercaptan that was first formed added to a second molecule of the hydrocarbon to form a sulphide.[68]

TABLE III.

Unsaturated hydrocarbon.	Yield of products (%).	
	Mercaptan.	Sulphide.
Ethylene	11	80
Propylene	7	90
1-Butene	23	6
Octene-1	9	35
*cyclo*Hexene	7	5

Böeseken and van der Linde found that hydrogen sulphide and isoprene react when heated in an autoclave in the presence of ferric oxide at temperatures below 96° C, mercaptans being formed, probably $Me_2C(SH)CH{=}CH_2$ and $Me_2C(SH)CH(SH)Me$.[69]

The patent literature discloses the use of various catalysts for the vapour-phase reaction of hydrogen sulphide and olefins: adsorbents, such as fuller's earth,[70] silica gel,[70] and clay,[71] at temperatures of 100° to 300° C; metallic sulphides (Ni, Fe, Co) at temperatures of 150° to 200° C,[72, 73] phosphoric acid on kieselguhr at temperatures of 175° to 315° C.[74] Badertsher, Coonradt, and Crawley have proposed utilizing the increased reactivity of branched-chain olefins for separating the olefins in hydrocarbon gases and producing mercaptans. They claim that by treating the gases with hydrogen sulphide at 25° to 175° C in the presence of the acids and thio-acids of phosphorus, the tertiary olefins are converted to *tert*-butyl and amyl mercaptans, whereas other saturated and unsaturated hydrocarbons are unaffected.[75] Terpenes also appear to react with hydrogen sulphide more readily than do the simple olefins.[76] According to Borglin and Ott, terpenes, such as pinene and turpentine or rosin, react with hydrogen sulphide at 80° C, or in the presence of acids (H_2SO_4, H_3PO_4) and bases ($Ca(OH)_2$), aluminium, metallic sulphides, etc., giving products containing mercaptans suitable for ore flotation or conversion into wetting agents.[77]

Effect of Ultra-violet Light.

Avery and Forbes found that under the action of ultra-violet light hydrogen sulphide reacts with chloromethanes (CH_2Cl_2, $CHCl_3$, CCl_4) at temperatures of 25° to −37° C, the products containing mercaptans,[78] and Vaughan and Rust have shown that under these conditions hydrogen sulphide also reacts with olefins and their derivatives. In the vapour phase the reaction is slow, but is accelerated by photo-sensitizers (*e.g.*, Me_2CO). The addition takes place contrary to Markownikoff's rule. Thus, when 0·044 mol of ethyl ethylene and 0·088 mol of hydrogen sulphide was irradiated in a quartz tube for 4 min at 0° C, 3·8 ml of reaction product was obtained containing 85 per cent of *n*-butyl mercaptan and 15 per cent of *n*-dibutyl sulphide. At −78° C the reaction was much slower. Methyl ethylene irradiated for 6 min at 0° C gave a 95 per cent yield of a product containing 65 per cent of *n*-propyl mercaptan and 35 per cent of *n*-dipropyl sulphide, whilst hexadiene-1 : 5 ($CH_2{=}CH{-}CH_2)_2$ reacted easily, giving high-polymer compounds.[79] Farmer, Shipley, and Naylor, who have studied this reaction in the presence of sulphur, in their investigation of the

mechanism of vulcanization, confirmed that the irradiation of mixtures of hydrogen sulphide and olefins results in the formation of the corresponding *n*-alkyl mercaptan and *n*-dialkyl sulphide by abnormal addition. In the absence of light, at about 140° C, small quantities of sulphur catalysed the addition of hydrogen sulphide to *iso*butylene and *cyclo*hexene, tertiary derivatives, including mercaptan and mono- and di-sulphides, being formed by normal addition. The disulphide was shown to be formed by the concurrent oxidation of mercaptan and reduction (hydrogenation) of the olefin,[80] as reported by Williams and Allen (*loc. cit.*). According to Hoeffelman and Berkenbosch, abnormal addition also takes place in the presence of peroxides which act as a catalyst, and of various metallic salts (Fe, Cr, Mn, etc.), which act as catalyst activators.[81]

Reaction between hydrogen sulphide and olefins can also be brought about at ordinary temperatures by the silent electric discharge. Losanitsch and Jovitschitsch found that ethylene and hydrogen sulphide were condensed by the silent discharge (3·5 amps, 70 volts) to a yellowish-red liquid of mercaptan-like odour and having the composition $(C_2H_4S)_6$, the reactions probably being $C_2H_4 + H_2S \longrightarrow CH_3CH_2SH$; $6CH_3CH_2SH \longrightarrow (C_2H_4S)_6 + 6H_2$. Some evidence for these reactions was that ethyl mercaptan when subjected to the silent discharge also gave the compound $(C_2H_4S)_6$. Acetylene and hydrogen sulphide gave a yellow malodorous product containing compounds of the composition $3C_2H_22C_2H_4S_4$, and $C_2H_23C_2H_4S_2$.[82]

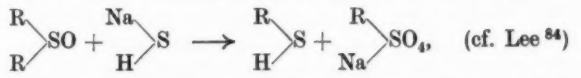
Liquid-phase Reaction in the Presence of Acids and Bases.

The addition of hydrogen sulphide to unsaturated hydrocarbons takes place in the liquid phase at atmospheric or slightly elevated temperatures in the presence of acids. The formation of mercaptans from unsaturated hydrocarbons derived from petroleum or natural gas in this way has been patented by Johansen.[83] According to Lee, *secondary* and *tertiary* alkyl esters, formed by treating material containing unsaturated hydrocarbons with sulphuric acid, react with hydrogen sulphide to form mercaptans and thioethers.[84] Bähr and Corr have patented the production of mercaptans from diolefins by reacting them with hydrogen sulphide at 50° to 100° C in the presence of acid phosphorus compounds.[85] Water-binding agents, such as acetic acid, may also be used at temperatures of 35° to 300° C (90° to 250° C in examples).[86, 87]

Alkalies apparently can also act as catalysts. According to a patent of the I.G. Farbenindustrie, hydrogen sulphide reacts with compounds of the general formula $RCH{=}CH_2$, at atmospheric temperature, but preferably at 100° to 300° C, in the presence of basic substances giving organic sulphides (*e.g.*, di-*iso*propyl sulphide, presumably with the intermediate formation of a mercaptan).[88] According to another patent of this company, when a mixture of hydrogen sulphide and acetylene is led through a solvent containing a small proportion of ammonia, or an alkali or alkaline-earth sulphide or polysulphide as catalyst at room temperature, ethyl mercaptan, vinylethyl sulphide, and ethane dithiol diethyl are formed.[89] Reference has already been made to the patent of Borglin and Ott [77] for the production of sulphur-containing terpene compounds from terpenes and hydrogen sulphide in the presence of acids and bases (*e.g.*, $Ca(OH)_2$). Disulphides

apparently can also be converted into mercaptans by boiling with aqueous sodium hydrogen sulphide.[90]

An investigation by the research staff of the National Benzole Co.[20] of the appearance of mercaptans in refined benzoles when, with the introduction of gum inhibitors less concentrated sulphuric acid was used for refining, showed that mercaptans were formed readily when the crude benzoles containing hydrogen sulphide were washed with acid. The maximum amounts of mercaptans were formed with 1 to 3 per cent by vol of acid of 78 to 82 per cent strength. With larger amounts of acid, or stronger acid, less mercaptans were produced, and free sulphur was formed by oxidation of the hydrogen sulphide. The mercaptan troubles disappeared immediately an alkali wash was given before treatment with acid.[91] No evidence was found that hydrogen sulphide reacted with constituents of the benzole under the usual conditions of storage. Mercaptans were also found in refined benzoles produced from gas-works (vertical-retort), crude benzoles recovered from purified gas, when soda or soda ash was added to the still in order to prevent the formation of sulphur dioxide and its resulting corrosion troubles. Laboratory tests confirmed that crude gas-works benzoles, after washing first with caustic soda and then with acid of 82 per cent strength, formed mercaptans when subsequently refluxed at about 80° C with caustic soda and sodium sulphide, or with caustic soda and iron filings, and in larger amount (0·01 per cent S as mercaptan) when refluxed with both sulphur (0·1 g/100 ml) and caustic soda. If the benzoles had not been washed previously with acid, mercaptans were formed only when both alkali and sulphur were present. Although the production of mercaptans from acid-washed benzoles could be explained by reactions of the type :—



no mercaptans were obtained when benzene solutions of unsaturated hydrocarbons (amylene, *cyclo*hexene, mono- and di-*cyclo*pentadiene, and indene) were refluxed with caustic soda and hydrogen sulphide or free sulphur before or after washing with acid, and the production of mercaptans from benzoles that had not been washed with acid was not explained.[20]

Kiemstedt has also drawn attention to the formation of mercaptans when crude benzoles containing hydrogen sulphide are washed with sulphuric acid. He found that the addition of hydrogen sulphide to amylene and hexylene in benzene takes place at room temperature with acid below 96 per cent strength acting as a catalyst.[92]

Thermal Decomposition of Mercaptans, Sulphides, and Disulphides.

Further information should be obtainable concerning the conditions under which hydrogen sulphide reacts with olefins from a study of the reverse reaction, the decomposition of mercaptans into hydrogen sulphide and olefins.

Sabatier and Mailhe found that when ethyl mercaptan, for example, was passed over a cadmium-sulphide catalyst at 320° to 330° C, ethyl sulphide

and hydrogen sulphide were formed. At 380° C ethylene and hydrogen sulphide were the main products, the general reactions being :—

$$2C_nH_{2n+1}SH = (C_nH_{2n+1})_2S + H_2S$$
$$(C_nH_{2n+1})_2S = 2C_nH_{2n} + H_2S$$ [93]

Faragher, Morrell, and Comay, who investigated the thermal decomposition of various kinds of sulphur compounds under cracking conditions, found that a vaporized solution of *iso*amyl mercaptan in naphtha, when subjected to a temperature of 496° C, decomposed into hydrogen sulphide, elementary sulphur, hydrocarbon gases, and a tarry residue. No sulphide or thiophen could be detected. Disulphides gave hydrogen sulphide, mercaptans, thioethers, and thiophen or its derivatives. From ethyl sulphide only hydrogen sulphide, mercaptans, and hydrocarbon gases were obtained, whilst *iso*amyl sulphide gave the same products together with some thiophen derivatives. Faragher, Morrell, and Comay also found that ethyl and propyl disulphides could be distilled without decomposition, but higher-molecular-weight disulphides decomposed during distillation. Butyl disulphide, for example, gave a trace of hydrogen sulphide, and heptyl mercaptan, and *iso*amyl disulphide gave a large quantity of hydrogen sulphide and about 9 per cent of sulphur as *iso*amyl mercaptan.[94] Elgin passed solutions of *n*-butyl mercaptan, *iso*butyl mercaptan, propyl sulphide, *iso*butyl sulphide, and thiophen in naphtha over a nickel catalyst at 300° C, and found under these conditions that hydrogen sulphide was evolved from both mercaptans and sulphides. The mercaptans were removed more readily than the sulphides [95] (Table IV).

TABLE IV.

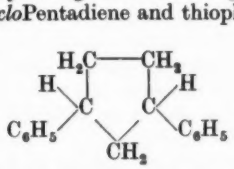
Sulphur compound in naphtha.	Rate of flow (cc/hr).	Sulphur content (% w/w).		Reduction in S (%).
		Initial.	Final.	
Butyl mercaptan . . .	100	0·375	0·028	93
„ „ . . .	200	0·375	0·079	79
*iso*Butyl mercaptan . .	100	0·374	0·105	72
Propyl sulphide . . .	100	0·393	0·309	21
*iso*Butyl sulphide . . .	100	0·388	0·323	17

Malisoff and Marks examined the thermal decomposition of solutions of *n*-propyl, *n*-butyl, *iso*butyl, *n*-amyl, *iso*amyl, *n*-heptyl, and benzyl mercaptans in various solvents at temperatures of 300° to 475° C and times of exposure of 8 to 181 sec. The amount of decomposition increased with rise of temperature and time of exposure. All the mercaptans on decomposition yielded hydrogen sulphide and an olefin. The branched-chain isomers were less stable than the straight-chain isomers, although only markedly so at high temperatures (475° C). The higher homologues are probably more stable than the lower mercaptans, although there was no marked difference. Benzyl mercaptan was less stable than the lower aliphatic mercaptans. The solvent apparently had an influence, benzene compared with straight-run naphtha promoting decomposition. *n*-Butyl sulphide in benzene solution was thermally stable at 400° C, slightly de-

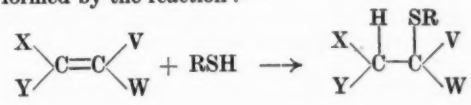
composed at 450° C, more so at 500° C, but even at 515° C with a 30 sec exposure, the conversion to hydrogen sulphide was only 20 per cent. The other product of reaction was butyl mercaptan. Benzene appeared to accelerate the reaction, and *n*-heptane to act as an inhibitor.[96] Trenner and Taylor found that ethyl mercaptan or sulphide was decomposed at 380° to 410° C and 50 to 400 mm pressure into hydrogen sulphide, ethylene, and polysulphides, an intermediate product (b.p. 481° to 495° C), possibly a dimercaptan ($C_2H_5SH{=}SHC_2H_5$), being isolated.[97] Similarly, propyl mercaptan decomposed at 405° to 435° C and 100 to 300 mm pressure into propylene and hydrogen sulphide.[98] Using a cadmium sulphide–zinc-sulphide–aluminium-oxide catalyst at 350° C, Wiezevich, Turner, and Frolich found that diethyl sulphide was the main product in the thermal decomposition of ethyl mercaptan.[99] The concurrent oxidation of mercaptans to disulphides and reduction (hydrogenation) of olefins has already been mentioned. High-molecular-weight mercaptans and sulphur when heated to about 175° C react forming first disulphides and hydrogen sulphide according to the equation $2RSH + S = R_2S_2 + H_2S$.[100]

Addition of Mercaptans to Unsaturated Hydrocarbons.

This reaction apparently was first investigated by Posner, who found that, in general, addition took place quite readily in the presence of glacial acetic acid and concentrated sulphuric acid at the normal temperature. The primary addition compounds, which were liquids, were identified as sulphides by oxidizing them to the corresponding well-crystallized sulphones. Little or no sulphur-containing derivatives could be obtained from ethylene or propylene, owing apparently to their slight solubility in the solvents used. Reaction also became more difficult with an increase in the number of phenyl groups in the unsaturated hydrocarbon, and neither stilbene nor diphenylpentadiene formed addition compounds. Styrene and phenylbutadiene, having only one phenyl group, still reacted with mercaptans. All other liquid and solid unsaturated hydrocarbons readily added on mercaptans. With some mercaptans and unsaturated hydrocarbons, reaction occurred at the normal temperature without any additional reagent. Styrene and thiophenol, for example, reacted without any further reagent in about ten days to give a clear liquid consisting mainly of $C_6H_5CH_2CH_2SC_6H_5$. *cyclo*Pentadiene and thiophenol reacted on standing for two months, giving



and with hexylene and diallyl the presence of a further reagent was found to be actually disadvantageous. Posner concluded that the addition compounds were formed by the reaction :—



and that with hydrocarbons having the double bond between two differently hydrided carbon atoms, the mercaptan radical (contrary to Markownikoff's rule) added to the most hydrided carbon atom. Of the various hydrocarbons with double bonds investigated, *cyclo*pentadiene gave a disulphone, whereas the others had only one reactive double bond. The yields of the primary addition compound obtained with hydrocarbons with two double bonds were usually small, whereas those from hydrocarbons with one double bond were good.[101]

Various investigations have been carried out since, to confirm Posner's conclusions. Ashworth and Burkhardt similarly found that thiophenol and styrene gave by abnormal addition $C_6H_5CH_2CH_2S_6CH_5$. The velocity of the reaction was followed in the light and in the dark. In the light, the reaction was practically complete in 1·5 days; in the dark, the reaction was still incomplete in 25·5 days. Light did not alter the direction of the addition.[102] Nicolet showed that the addition of benzyl- and *p*-tolyl mercaptans to αβ-unsaturated diketones, which took place readily at 100° C, was also abnormal.[103] Ipatieff, Pines, and Friedman found that in the absence of catalysts thiophenol added to aliphatic olefins contrary to Markownikoff's rule. The addition was also abnormal in the presence of phosphoric acid as catalyst, but in the presence of sulphuric acid, the normal alkyl product was obtained, and not the abnormal as reported by Posner.[104] Ipatieff and Friedman found that aliphatic mercaptans also added to olefins contrary to Markownikoff's rule under varying conditions of temperature (room to 100° C) and pressure in the absence of catalysts, whereas hydrogen sulphide added according to the rule. The mercaptans added more readily than hydrogen sulphide (100° to 200° C).[105]

Further light was thrown on this reaction when Jones and Reid,[68] following the work of Kharasch and his co-workers [106] on the effect of peroxides on the addition of halogen acids to ethylenic compounds, found that the addition of mercaptans to these compounds was even more sensitive to the effect of peroxides. No addition occurred with carefully purified reagents. Sulphur catalysed the normal addition, and peroxides the abnormal. The quantities of peroxides usually present in the hydrocarbons render the abnormal addition difficult to suppress. Light probably serves merely to accentuate the peroxide effect.[106]

B P 532,676 covers the formation of *sec*- and *tert*-mercaptans and thioethers from unsaturated hydrocarbons and mercaptans of the general formula RSH, where R may be hydrogen or an organic radical, in the presence of peroxides and metallic salts of strong inorganic acids.[107]

Reference has already been made to the preparation of addition compounds from ethyl mercaptan and mono- and di-*cyclo*pentadiene and other unsaturated compounds by Kruber and Schade.[34] According to Bruson and Riener, reaction between di*cyclo*pentadiene and mercaptans gives a dihydronordi*cyclo*pentadienyl sulphide of structure A–S–R, where A is an alkyl or aryl group and R is the dihydronordi*cyclo*pentadienyl radical,[108] whilst according to Coffman, dienes and dithiols form polymeric sulphides on heating to 100° to 150° C, or exposure to a mercury arc until polymerization has proceeded to the desired stage.[109]

Other Reactions of Mercaptans and Disulphides.

Another important characteristic of mercaptans and disulphides is the ease with which they can be converted the one into the other by oxidation and reduction :—

$$2RSH \underset{H_2}{\overset{O}{\rightleftharpoons}} R_2S_2$$

Oxidation of mercaptans to disulphides by air occurs readily, especially in alkaline solution. Oxidation is also effected by sulphur.[46] Strong oxidizing agents convert mercaptans to thiosulphonic esters, alkyl sulphonic acids, and other products The reductive cleavage of disulphides has been used for the dehydrogenation of tetralin and other hydro-aromatic hydrocarbons.[110]

The oxidation of mercaptans to the almost odourless disulphides is the basis of the older "sweetening" processes for their elimination from petroleum distillates—doctor treatment, hypochlorite, copper-chloride processes, etc., and the various modifications. The total sulphur was not reduced. Owing mainly to the deleterious effect of disulphides on the lead response of petrols, recent processes, which have been surveyed in a previous report,[111] aim at the removal of the mercaptans.

Summary and Discussion.

A survey of the literature on the reactions of sulphur, hydrogen sulphide, and mercaptans with unsaturated hydrocarbons shows that sulphur commences to react with some unsaturated hydrocarbons at temperatures below 100° C. The primary reaction is the formation of polysulphides. These sulphur compounds break up at higher temperatures to give alkyl mercaptans, dialkyl sulphides, and hydrogen sulphide, which therefore are secondary and not primary products of the reaction as assumed hitherto. Thiophen derivatives are also formed from some unsaturated hydrocarbons at temperatures of 150° to 200° C. Simultaneous condensation or polymerization of the olefin and products of reaction is also liable to occur. Basic substances, *e.g.*, ammonia, piperidine, amines, apparently catalyse the formation of the polysulphides, and act as "sulphur carriers." Practical application is made of this catalytic effect in the vulcanization of rubber. The reaction of sulphur with aromatic, paraffinic, and naphthenic hydrocarbons occurs only at appreciably higher temperatures.

Hydrogen sulphide apparently does not react with unsaturated hydrocarbons as readily as sulphur. In the absence of catalysts, other than the metal of the vessel used, there is appreciable reaction in the vapour phase with *n*-olefins at temperatures of 150° to 200° C, and with branched-chain olefins at temperatures of 100° to 150° C. In the equilibrium :—

$$\left.\begin{matrix}H\\H\end{matrix}\right\rangle S + C_nH_{2n} \rightleftharpoons C_nH_{2n+1}SH,$$

low temperatures favour the formation of mercaptans and high temperatures the formation of hydrogen sulphide and olefin. At 300° C, however, an appreciable amount of mercaptan is still present under equilibrium conditions. The mercaptan formed reacts readily with more of the olefin

to form sulphides, the proportions of mercaptans and sulphides obtained depending on whether the hydrogen sulphide or the olefin is in excess. Elementary sulphur acts as a catalyst to the formation of mercaptans, and various other catalysts, such as adsorbents and metallic sulphides, have been used to speed up the reaction at lower temperatures. Under the action of ultra-violet light, reaction occurs at temperatures below 0° C. The reaction is not sensitive to the "peroxide effect", and the addition of the hydrogen sulphide is normal, *i.e.*, in accordance with Markownikoff's rule, except under the action of light, or when fairly large amounts of peroxides are added as catalysts.

Reaction of hydrogen sulphide with unsaturated hydrocarbons to form mercaptans occurs readily in the liquid phase in the presence of acids, alkyl sulphonic esters, and bases. Bases possibly favour the formation of sulphides.

Addition of mercaptans to unsaturated hydrocarbons with the formation of sulphides takes place much more readily than that of hydrogen sulphide. Addition of mercaptans to some unsaturated hydrocarbons, *e.g.*, *cyclo*-pentadiene and styrene, can take place at atmospheric temperature. Reaction, however, is slow at this temperature and may take days or even months for completion. The rate of reaction is greatly accelerated by acids. In the absence of catalysts, or in the presence of only weak acids and of light, the addition is abnormal. In the presence of sulphuric acid, the normal products are obtained. Sulphur also catalyses the normal addition. The reaction is very sensitive to the peroxide effect, and the quantities usually present render the abnormal addition difficult to suppress.

Mercaptans are very readily oxidized by air to disulphides, whilst the latter in the presence of hydro-aromatic and other easily oxidizable hydrocarbons readily undergo reductive cleavage to mercaptans.

The light thrown on the problem of the formation of sulphur-containing sludge in wash oils may now be considered. Elementary sulphur, in view of its greater activity on unsaturated hydrocarbons compared with that of hydrogen sulphide, appears to be the form of sulphur most likely to be responsible. For the same reason this sulphur would be expected to be formed by oxidation of hydrogen sulphide, which reaction is known to occur readily in the presence of iron and its compounds, rather than by the oxidation of mercaptans or other products of the addition of hydrogen sulphide to unsaturated hydrocarbons (Demann and Brösse). Starting therefore with sulphur, the following mechanism based on the data, etc., disclosed in the literature and in accordance with most plant observations, is suggested :—

(1) Addition of sulphur to unsaturated hydrocarbons to form polysulphides. This reaction, which apparently is catalysed by ammonia, takes place at low temperatures (below 100° C).

(2) Decomposition of the polysulphides to mercaptans, sulphides, disulphides, and hydrogen sulphide. This reaction occurs at about 140° C (*i.e.*, in the pre-heater and stripping-still).

(3) Addition of the mercaptans to more of the unsaturated hydrocarbons at this and lower temperatures (*i.e.*, during cooling of the oil from the stripping-still) to form sulphides and at higher temperatures

to form thiophen derivatives (Kattwinkel's heterocyclic sulphur compounds). These reactions are catalysed by the elementary sulphur.

(4) Condensation and polymerization of more of the unsaturated hydrocarbons with the mercaptans, sulphides, and thiophen derivatives, as well as co-polymerization with products of the oxidation of unsaturated hydrocarbons to form material with sulphur and oxygen acting as linking units, as in certain plastics, rubber, etc. This occurs when oil containing these products is again heated in the pre-heater and stripping-still. This part of the scheme is an extension of that due to Kattwinkel.

The catalytic effect of ammonia on the reactions receives some support from the plant survey of the Benzole Technical Committee where it was observed that at coke-oven works sludging appeared to be worst at plants in which ammonia was allowed to "slip", whereas at gas-works, in the absence of hydrogen sulphide, the reverse was observed.[112]

Since phenols are not known to inhibit the vapour-phase oxidation of hydrogen sulphide, or any of the liquid-phase sulphur reactions indicated above, but only purely oxidative reactions, it is to be expected that sludge inhibitors will be far less effective (if at all) at coke-oven works than at gas-works.

The various ways in which hydrogen sulphide and mercaptans can be formed during the final distillation of benzoles may be summarized as follows :—

(1) Reduction of disulphides to mercaptans.

(2) Action of sulphur on unsaturated hydrocarbons to give both hydrogen sulphide and mercaptans (as well as sulphides and disulphides).

(3) Thermal decomposition of disulphides, sulphides, and other sulphur compounds to give both hydrogen sulphide and mercaptans.

Reaction (1) occurs at the lowest temperature (below 80° C); then reaction (2) at temperatures above 80° C; and lastly, reaction (3) only at comparatively high temperatures, 150° to 250° C.

In the investigation of the "Causes of Mercaptan Formation in Benzole and Methods of Removal", it was found that crude gas-works vertical-retort benzoles, after washing with caustic soda and 82 per cent sulphuric acid readily gave mercaptans on subsequently distilling with caustic soda and sodium hydrogen sulphide, or with caustic soda and sulphur, or with caustic soda and iron filings, whereas no mercaptans could be obtained when "synthetic crudes" prepared from pure aromatic and unsaturated hydrocarbons were treated in the same way. One explanation is that some other more reactive unsaturated hydrocarbon was present in the vertical-retort benzole that reacted at distillation temperatures (80° to 160° C) with the alkali and sulphur. A more probable explanation, however, in the light of this survey, and one that explains all the facts, is that mercaptans were formed by reaction (1) above from disulphides present in the vertical-retort benzoles, but absent from the synthetic benzoles. In support of this suggestion it is pointed out that low-gravity (vertical-retort) benzoles,

both crude and refined, have been found to contain the highest amounts of disulphides.[113]

Further promising lines of investigation of both the problem of the sludging of wash oils and of mercaptan formation during refining are indicated.

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THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, December 8, 1948. Mr H. Hyams (Vice-President) was in the Chair.

The Secretary (Mr D. A. Hough) read the notice convening the meeting and the Minutes of the preceding Ordinary General Meeting held on November 10, 1948, were read, confirmed, and signed.

The Secretary read the names of those elected to membership since the previous meeting.

The Chairman: The main purpose of this meeting is to hear a paper on the subject of evaporation losses at marketing installations. I do not think that Mr Sarjeant, the author, needs any special introduction, because he is already well known to petroleum engineers largely on account of the particular interest he has taken during his very long association with the Shell Group in the problem which he presents in his paper this evening.

We in the Institute are really fortunate in having an expert of Mr Sarjeant's calibre to give us this paper. We are attempting to cater for the requirements of those in the industry in the widest possible field, and we have here for the first time for many years a paper which is out of the ordinary. There has been a tendency, and possibly there have been complaints, to limit ourselves to papers dealing with the chemical, chemical engineering, refinery practice, production, and geological sides of our industry, but we now have a paper for those concerned with marketing operations wherever oil of all kinds is stored and distributed. We therefore extend a warm welcome to Mr Sarjeant.

The following paper was then presented:

EVAPORATION LOSSES AT MARKETING INSTALLATIONS.

By R. L. Sarjeant.*

The question of evaporation losses from gasoline in storage at marketing installations is doubtless in the mind of all those concerned with such storage. It is surprising, however, how few people really appreciate the magnitude of such losses, and by what simple means they may be quite materially reduced. Marketing installations are referred to advisedly, as it is at these, rather than at refineries, that such losses are of importance. After all, the aim at refineries should be to make up products and blends in

* Shell Petroleum Co., Ltd.

accordance with market requirements, and get rid of them as they are made. Although this Utopian state of affairs can rarely, if ever, be fully achieved in practice, the fact remains that marketing installations essentially involve long-term storage of products to a far greater degree than refineries. Again, generally speaking, at refineries products are "duty free", whereas at very many marketing installations gasoline in storage has already paid duty, so that from the financial angle losses from marketing installations may easily be two or three times as much as in the case of refineries.

Very little appears to have been published on the subject, and what little there is emanates in general from the manufacturers of so-called vapour-conservation devices. This is not to suggest by any means that data put forward by them is in any way misleading—on the contrary, it is in general accurate and helpful, but it is only natural that it should emphasize points that are supporting factors from their own sales angle, and equally natural that other methods of tackling the problem are not given undue prominence. In these circumstances one is faced with the alternative of whole-hearted acceptance of their recommendations, or the initiation of independent investigation of the problem of evaporation losses as a whole.

So far as the Group to which the author belongs is concerned, matters came to a head in the early days of the introduction of bulk storage of gasoline in the Far East, losses from certain tankage in Japan being so high as to cause grave concern. Preliminary investigations were initiated by simply suspending an ordinary maximum–minimum thermometer in the vapour space of a tank, and thus taking daily readings, which immediately revealed a much wider range of temperature than had been anticipated, a daily variation between day and night temperatures of 60°, 65°, and even 70° F being by no means uncommon. It was ultimately decided that the problem warranted treatment on a more comprehensive scale, and recording thermometers and pressure gauges of the weekly type (provided with seven-day clock mechanism) were provided for collecting physical data, together with Chenicek–Whitman apparatus for ascertaining the actual evaporation losses from tanks. For the benefit of those who are not familiar with the principle of this apparatus, it is pointed out that when loss by evaporation occurs, naturally the lighter fractions are the first to be driven off, and this has a marked effect on the vapour pressure of the gasoline. In practice, a sample of the gasoline originally in the tank is passed through the apparatus, in which under carefully controlled conditions successive small percentages are evaporated off—say 0·25, 0·5, 0·75 per cent, and so on, and at each stage the vapour pressure of the remaining gasoline is carefully ascertained. From these results an original vapour pressure–percentage evaporation curve is plotted, vertical ordinates representing vapour pressure. From time to time as the test proceeds, further samples are taken from the tank under test, and passed through the same process, and the results plotted on the same sheet. Ultimately the chart will embody a series of such vapour pressure–percentage evaporation curves, comprising parallel straight lines, and the horizontal distance between the original curve and any one of the subsequent curves gives the percentage evaporation loss to the date of taking the sample from which the

latter curve has been obtained. Most meticulous care must be taken in withdrawing samples from the tank to ensure that they are truly representative, and that none of the lighter fractions are inadvertently lost either during sampling or transport to the laboratory. One great advantage of the Chenicek–Whitman method is that there is no need to put the tank out of commission—withdrawals from the tank will not affect the results, and so long as no fresh supplies of gasoline are introduced into the tank, which would, of course, alter the vapour pressure of the contents, the series of readings may be continued.

We will now turn to the theory of evaporation losses and a consideration of different methods of reducing them.

What do we mean by evaporation loss? For all practical purposes, it is the loss due to what we call "breathing" of storage tanks. Assume a tank to be partly full of gasoline, the space above the gasoline will comprise a mixture of air and gasoline vapour. During the day the rise of temperature causes this air–vapour mixture to expand, and a considerable volume will be expelled to atmosphere through the tank vents. During the night the temperature falls, and the consequent fall of pressure in the tank vapour space results in a quantity of pure air being drawn in through the vacuum valves in the tank vents. This fresh air in turn becomes saturated with gasoline vapour, and the whole cycle is repeated next day. Thus we experience a daily "breathe", in which each day a mixture of air and vapour is expelled from the tank, and each night fresh air is drawn into the tank, and it is this loss which we refer to as evaporation loss.

What is the magnitude of such losses? The actual loss in the case of a freely vented tank, it will at once be seen, depends on three factors, viz.:

(*a*) the volume of the vapour space;
(*b*) the range of temperature; and
(*c*) the percentage of gasoline vapour in the air–vapour mixture expelled from the tank.

With regard to (*a*) it is suggested that under average conditions throughout the year, a tank will be half full of gasoline. That is to say, when the tank is nearly empty, it will be replenished, and after receipt of a fresh cargo it will be nearly full, so that in any complete cycle the average condition will be approximately half full.

With regard to (*b*), the range of temperature in the vapour space, it might at first be thought that this would show marked differences in different parts of the world, dependent on latitude and general climatic conditions. It is perfectly true that if records over short periods are compared, the temperature range in different localities will be found to vary widely, but from records taken over a number of years, the conclusion has been reached that the *average* daily temperature range throughout the year is approximately 30° F, both in the tropics and in temperate zones. This will probably cause some surprise. The fact of the case is that in the tropics long periods are experienced in which the temperature range is of this order, ranging perhaps from 25° to 35° F, with exceptional days in which the daily range may be as low as 15° to 20° F, and in other periods as high as 40° F and even more.

The dotted-line curves on Figs. 1, 2, and 3 illustrate this point, representing average range, maximum range, and minimum range respectively.

In temperate climates, on the other hand, whereas there are long periods during which the range may be very small—of the order of 10° F—these are compensated by periods, extending over several weeks in the late spring and again in the early autumn, when there may be a touch of frost during the night and yet the days may be warm and sunny, when the temperature range in the vapour space is very wide indeed, a figure of 60°, 65°, and even

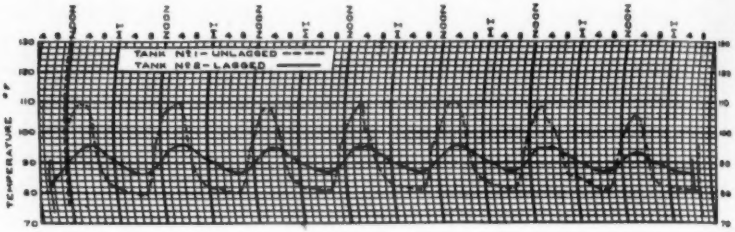

FIG. 1.

TANK NO. 1—98 FT DIAM × 14·65 FT HIGH.
TANK NO. 2—91 FT DIAM × 14·65 FT HIGH.
BOTH TANKS FILLED TO 65 PER CENT CAPACITY.

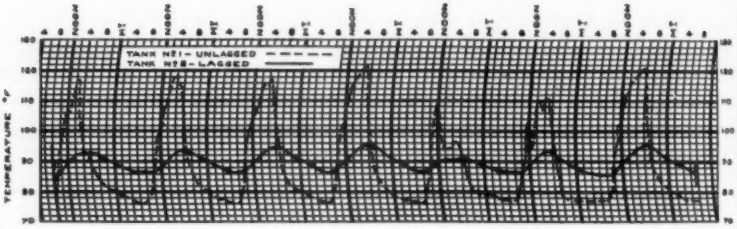

FIG. 2.

TANK NO. 1—98 FT DIAM × 14·65 FT HIGH.
TANK NO. 2—91 FT DIAM × 14·65 FT HIGH.
BOTH TANKS FILLED TO 65 PER CENT CAPACITY.

70° F being by no means uncommon. Fig. 4 obtained from a tank in the U.K. in early June illustrates this point. Data have been collected at intervals over a number of years, dating right back to 1930, in the early days as previously mentioned by suspending a simple maximum–minimum thermometer reset daily in the vapour spaces of various tanks, and in later years by suspending a seven-day recording instrument in the vapour spaces, covering areas as wide apart as the United Kingdom, Japan, Australia, Singapore, and Colombo, and the conclusion has been reached that an *average* daily variation of 30° F in the vapour space of exposed above-ground tanks, is a reasonable assumption for calculation purposes. This is not to suggest that 30° F represents the maximum average annual range of temperature in the vapour space of a tank, but rather a safe

minimum figure to adopt for calculation purposes. Undoubtedly in northern India, the Middle East, and North America, the range will be wider still, and in the author's view it would be well worth while for operating companies

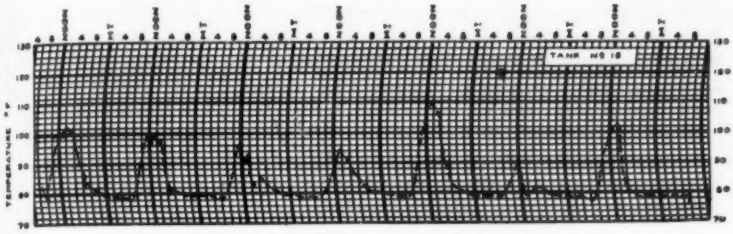

FIG. 3.

TANK NO. 16—91 FT DIAM × 33·75 FT HIGH.
TANK FILLED TO 50 PER CENT CAPACITY. ROOF UNLAGGED.

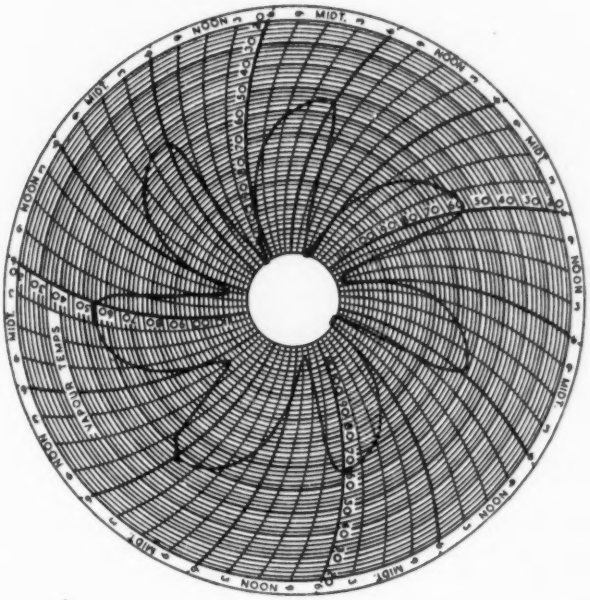

FIG. 4.

TEMPERATURE RECORD FROM UNLAGGED TANK IN THE U.K. EARLY JUNE.
TANK 91 FT DIAM × 33·75 FT HIGH. TANK FULL.

to collect such information from all areas under their control. The results cannot fail to be illuminating, and enable this question of evaporation loss and alternative remedial measures to be tackled with confidence.

With regard to (*c*), the percentage of gasoline vapour in the air–vapour mixture in the vapour space of the tank, this is, of course, a function of the vapour pressure of the spirit stored, and its temperature. The calculation of this percentage is based on Dalton's law of partial pressures, as follows. If we take a closed gas-tight vessel containing air at atmospheric pressure, with an inner sealed vessel containing gasoline, and devise means for rupturing this inner vessel thus setting free the gasoline, what will happen? Partial evaporation will take place, and, provided that there is sufficient liquid gasoline present to ensure that it does not all evaporate, a state of

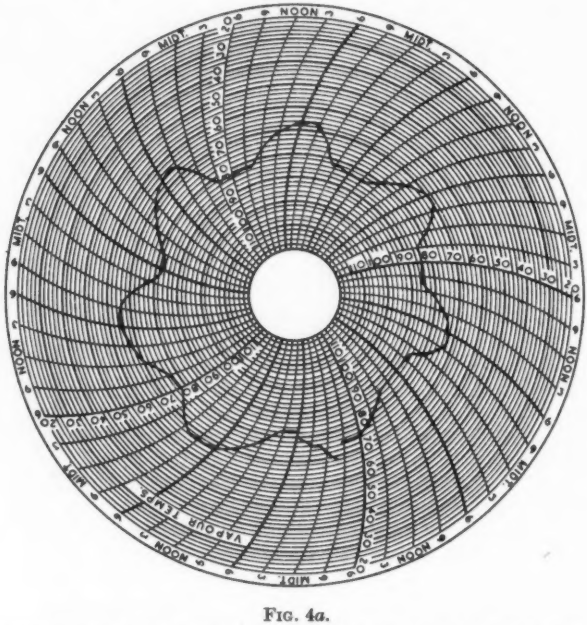

FIG. 4*a*.

TEMPERATURE RECORD FROM LAGGED TANK IN THE U.K. EARLY JUNE.
TANK 91 FT DIAM × 33·75 FT HIGH. TANK FULL.

equilibrium will be reached when the total pressure inside the container is equal to the original atmospheric pressure of the air content, plus the vapour pressure of the gasoline at the temperature of the gasoline at the time of the experiment. In other words, if the vapour pressure at that temperature were, say, 5 p.s.i., the total pressure in the container will be 19·7 lb, *i.e.*, atmospheric pressure 14·7 lb plus vapour pressure 5 lb. If, instead of being sealed, the container is freely vented to atmosphere, the release of the gasoline will again result in its vapour pressure tending to raise the pressure in the container, and the effect will be to drive out part of the air, or a mixture of air and vapour, from the container, until a state of equilibrium is reached when the total pressure in the container is 14·7 p.s.i., 5 lb

of which is due to the vapour pressure of the gasoline. In effect, part of the air has been exhausted from the container, and the contents of the vapour space will be $\frac{9{\cdot}7}{14{\cdot}7}$ air and $\frac{5}{14{\cdot}7}$ gasoline vapour. All we need, therefore, to determine the proportion of pure gasoline vapour in the vapour space of a tank, under saturation conditions, is the vapour pressure of the gasoline and the temperature of the liquid gasoline.

We are now in a position to calculate our breathing losses from first principles, based on the fundamental laws of gases, viz., $\frac{PV}{T}$ = constant, where P = pressure in absolute units, V = volume of air vapour mixture, T = absolute temperature.

In the case of a freely vented tank, P of course is constant, and under varying temperature conditions we get

$$\frac{V1}{T1} = \frac{V2}{T2}$$

or $V_2 - V_1$, the increase in volume due to the temperature change, or in other words the volume of " breathe " $= \frac{V1(T2 - T1)}{T1}$.

If, under tropical conditions, for example, $T1$ is 80° F or say 540° F abs, with a range of temperature of 30° F, we get volume of daily " breathe " $= \frac{V1 \times 30}{540} = \frac{V1}{18}$.

In the case of the larger storage tanks, under average operating conditions, *i.e.*, with the tank half full of gasoline, $V1$, the volume of the vapour space, may be of the order of 280,000 cu. ft, in which case the average daily breathe will be over 15,000 cu. ft of air–vapour mixture. As we have assumed tropical conditions, we may take the temperature of the liquid gasoline to be of the order of 80° F, and assuming that it is motor spirit having a vapour pressure of 10 lb Reid at 100° F the percentage of pure gasoline vapour in the air–vapour mixture under saturated conditions will be 46·1, so that the daily breathe of gasoline vapour will be $\frac{15000 \times 46{\cdot}1}{100}$ = 6915 cu. ft. It is the lighter fractions, of course, which are lost—those in the pentane–heptane range, for which we may take 34 cu. ft vapour = 1 gal liquid.

Thus, a tank of this size, *under freely vented conditions*, would lose over 200 gal daily—a truly alarming figure.

What can be done to reduce such losses? In the first place, instead of allowing the tank to vent freely, pressure–vacuum valves are fitted to the vents, to prevent vapour being expelled until a predetermined pressure is reached in the vapour space, and to prevent air being drawn in until a predetermined vacuum is reached. In the Group to which the author belongs, tanks are designed for 8-in water-gauge pressure and 2½-in water-gauge vacuum. What is the effect of this?

Again, taking $\frac{P1\,V1}{T1} = \frac{P2\,V2}{T2}$, it will be appreciated that within the

range of operation of the pressure–vacuum valves, $V1 = V2$, so we get $\frac{P1}{T1} = \frac{P2}{T2}$, or $T2 - T1 = \frac{(P2 - P1)}{P1} T1$.

As our valves are set to inches water gauge, it is convenient to express atmospheric pressure in similar units. One atmosphere may be taken as 34 ft water, or 408-in water gauge, so that our valves are set to work between $408 + 8\text{-in} = 416\text{-in}$, and $408 - 2{\cdot}5 = 405{\cdot}5$ in, and we get $T_2 - T_1 = \frac{10{\cdot}5}{405{\cdot}5} \times 540 = 14°$ F.

This means that the range of 14° F is looked after by the pressure-vacuum valves, and within that range of 14° F no breathing will occur, and there will be no loss. As our total temperature range is 30° F, we have practically halved our losses by arranging for our tanks to operate between 8-in water-gauge pressure and $2\frac{1}{2}$-in water-gauge vacuum.

What more can we do? It will be appreciated that the volume of daily "breathe" is directly proportional to (*a*) the volume of the vapour space

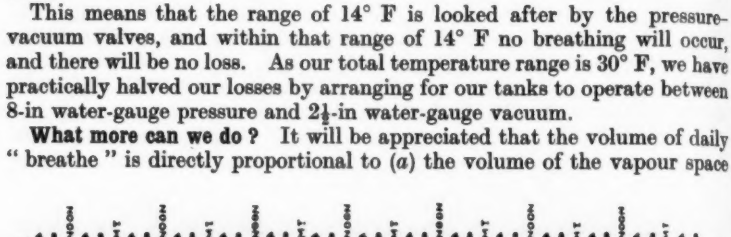

FIG. 5.

TANK 15 (LAGGED) 91 FT DIAM × 38·5 FT HIGH.
TANK 16 (UNLAGGED) 91 FT DIAM × 33·75 FT HIGH.
BOTH TANKS FILLED TO 25 PER CENT CAPACITY.

and (*b*) the temperature range, so that further savings can be achieved if we can reduce either—or both. An obvious answer in the case of the latter is to lag the tank roof, thus reducing the heating effect of the midday sun. This is markedly effective, particularly when the level of gasoline in the tank is high—in fact, when the tank is some 65 per cent full and upwards the temperature range is less than 14° F, so that no breathing occurs and losses are nil. As the gasoline level is reduced, the effect of the sun's rays on the shell of the tank morning and evening is to cause a temperature range in excess of 14° F, and, in fact, when the tank is nearly empty there is very little benefit from the lagging. Figs. 1 and 5 illustrate this point. Under all-round average working conditions it is found that the provision of lagging on the tank roofs reduces our residual losses by fully 50 per cent, so that in round figures the setting of our present vacuum valves saves approximately 50 per cent of our losses, the provision of lagging on the roof save about half of the remaining loss, and we are left with only 25 per cent of what the losses would be from a freely vented tank. In the case of the larger tanks referred to above it will be seen that the saving amounts to no

less than 150 g.p.d. under tropical storage conditions—and this from a single tank.

This seems an appropriate moment to refer to American practice. Cone-roof tanks there are normally made to A.P.I. specification, which only provides for 1-in pressure and 1-in vacuum. It is suggested that it is quite impracticable to design relief valves, or pressure-vacuum valves, that will operate at such low pressures and still be truly gas-tight in the closed position. Such valves in the case of A.P.I. tanks act merely as draught excluders, and prevent exaggerated losses which would otherwise be caused by winds blowing across the tank roofs, which in the absence of some such valves would produce an eductor effect. Such tanks are, from the breathing angle, to all intents and purposes freely vented, and breathing losses are correspondingly high. It is for this reason that so-called vapour-conservation devices such as breather roofs, balloon roofs, gasometer roofs, vapour-spheres, and the like are popular—and quite rightly so—in the U.S.A. After all, if the losses (in the case of the larger tanks previously referred to) are of the order of 200 g.p.d., it pays handsomely to invest considerable capital sums in equipment to reduce such losses. With the lagged pressure-roof tanks, on the other hand, the remaining margin of loss is so small that the capital cost of such devices cannot be justified by the potential savings.

The other factor mentioned that governs the magnitude of the breathing loss is the volume of the vapour space, as the loss is directly proportional to this volume. This can be tackled in two ways: (*a*) by replacing any gasoline taken out of the tank by an equal volume of water, thus maintaining the gasoline level constant at or about the top of the tank shell and restricting the vapour space practically to the volume of the conical roof, and (*b*) by the provision of a floating roof, which practically eliminates the vapour space. The former alternative has been tried out, and earlier results were disappointing, losses being actually higher than from a tank operated normally. This was found to be due to a misunderstanding on the part of operators, who, having filled off several hundred tons of gasoline to service tanks, bulk vehicles, and/or drums and other packages, then proceeded to pump water into the tank to restore the gasoline level. This lowering and subsequent restoration of the gasoline level produced a definite pumping effect, fresh air being drawn in through the vents as the gasoline was drawn off, and a mixture of air and vapour being expelled when the level was restored by pumping in water. The artificial breathing thus resulting completely nullified the anticipated savings. This was subsequently overcome by providing a high-level discharge for gasoline near the top of the tank shell, and a low-level connexion for the introduction of water. On pumping in water, gasoline overflowed through the high-level discharge, and with a tank of the order of 40 ft high, this provided an ample gravity head for the filling of containers, bulk vehicles, etc. This proved very successful. Two tanks in Hong Kong, both some 78 ft diameter and 40 ft high, were selected, one being operated normally and the other arranged for high-level discharge and so-called deep-water bottom. Over a period of twelve months, during which precautions were taken to ensure that the throughput of both tanks was as nearly as possible the same, the loss from the deep-water-bottom tank was almost exactly 25 per cent of that from the normally operated tank. Unfortunately, water supplies

are not over plentiful at many installations and, moreover, the use of water bottoms with certain gasolines—notably aviation spirit—was subsequently banned, so that this practice had to be abandoned.

The second alternative, the floating roof, has found favour in many areas, and at first sight this might be assumed to be the complete answer to the problem. Unfortunately this is not so. The floating roof proper is made smaller in diameter than the tank shell, the annular space between floating roof and shell being closed by long steel shoes constrained to bear against the shell of the tank, with a flexible seal connecting the top of the shoes to the rim of the floating roof. This narrow annular space, some 8 to 10 in in width, is subject to the rays of the sun except during the middle of the day when the latter is directly overhead, and although no records have been taken it is evident that the temperature in this annular space will be relatively high, resulting in loss through the seal vent. Added to this, as gasoline is drawn from the tank and the roof thus lowered, it leaves the inside of the shell wet with gasoline, which is at once evaporated off. In the aggregate it is found that from the evaporation loss angle, the floating roof is no better than the lagged pressure roof (by " pressure " 8-in water gauge is meant), but where the floating roof scores is from the point of view of filling losses. It will be appreciated that if, say, 10,000 cu.m. of gasoline is introduced into a fixed roof tank, 10,000 cu.m. of air–vapour mixture must be expelled through the tank vents. With the floating roof this particular loss is entirely eliminated, and it is a matter of simple economics to relate the saving thereby achieved to the additional cost of the floating roof, from which it is found that this extra cost is justified provided that the throughput of the tank per annum is 600 per cent of its capacity.

The above suggested method of calculating losses from first principles is based on certain assumptions which merit examination. Here we are treading on rather difficult ground, and the author put the following points forward rather as a basis for discussion, and in the hope that those better qualified than he will contribute their views.

I. Boyle law and Charles law are true for perfect gases, which the air–vapour mixture is certainly not—nor is any allowance made for varying atmospheric conditions, notably humidity. With regard to the first point, it is suggested that within the pressure range in question, varying between only a few inches water gauge above and below atmospheric pressure, the error will be negligible, bearing in mind that complete scientific accuracy is not the aim, but rather the development of a practical working hypothesis to enable one to visualize the profitability of various methods of reducing evaporation losses *under average working conditions*.

II. In calculating the percentage of pure gasoline vapour in the vapour space of a tank, complete saturation is assumed. Most authorities suggest that this is true, but the author feels that the point needs further investigation. It is suggested that when a tank is nearly full and the volume of " breathe " is small, the assumption may be a safe one, but that when a volume of fresh air of the order of 15,000 cu. ft or more is drawn in overnight, it is possible that complete saturation will not have been reached by the time outward breathing commences.

III. In calculating the percentage of pure gasoline vapour in the vapour space of a tank, the temperature of the liquid gasoline in the tank, even at

the surface, is assumed constant, and to be unaffected by variations in the temperature of the vapour space above it. This is a point which has given rise to arguments in the past, some maintaining that there is a quite appreciable temperature rise, with a corresponding rise of vapour pressure, resulting in a richer mixture in the vapour space, and increased breathing losses. Determination of the temperature at the absolute surface of the liquid is difficult, and it is suggested that the simplest method of approach is as follows. Using the formula $\frac{P1\,V1}{T1} = \frac{P2\,V2}{T2}$, if we can obtain pressure and temperature curves in the vapour space of a tank under such conditions

FIG. 6.

TEMPERATURE AND CORRESPONDING PRESSURE RECORDS FROM VAPOUR SPACE OF A LAGGED ROOF TANK, 91 FT DIAM × 38·5 FT HIGH.

that the pressure range resulting from the temperature variations is within the setting of our pressure–vacuum valves, the volume will be constant, and we get $\frac{P1}{T1} = \frac{P2}{T2}$. This will only hold good if there is no rise of temperature at the gasoline surface, whereas if there *is* any such rise, the formula becomes $\frac{P1}{T1} = \frac{P2}{T2} + p$, p being the increase in vapour pressure due to the rise in temperature at the liquid surface. Unfortunately, records of pressure in the vapour spaces of tanks are somewhat meagre, as although pressure recorders were originally provided, their regular use was discontinued as pumping operations into and out of tankage rendered them meaningless. From those available, however, Fig. 6 has been selected as representative of the above conditions, and the recorded pressures exceed the calculated pressures by something less than 1 in water gauge on the

average, representing a rise of temperature at the gasoline surface of the order of $\frac{1}{8}$° F, which is negligible. It thus appears that the temperature gradient is in the main confined to the vapour space. It is also suggested that any tendency to increase of temperature at the liquid surface is retarded by the evaporative cooling effect at the surface. The particular tank in question had a lagged roof (evidenced by the restricted range of temperature in the vapour space). It is possible that with an unlagged roof conditions might be different, as the steel sheets comprising the roof will be at a much higher temperature, possibly sufficient to raise the temperature of the surface of the gasoline, particularly when the tank is nearly full, by direct variation. On the other hand, with exposed horizontal cylindrical tanks, we have records of pressures in the vapour space up to 2·8 lb higher than calculated from the vapour-space temperature range, particularly when such tanks are nearly full. This is in part due to direct heating of the liquid through the upper half of the periphery of the tank, and in part to direct radiation from that part of the tank shell above the liquid level, from which it is separated by a matter of a few inches only, as compared with many feet in the case of a vertical cone-roof tank, with the exception of the region round the periphery.

IV. The influence of the tank proportions on evaporation losses appears to merit further investigation. Present indications are that losses from large-diameter shallow tanks (such as are employed on ground of low-bearing capacity) are higher than calculated by the above methods. This lends some support to the suggestion above that gasoline surface temperatures are affected by direct radiation from the roof, as with such tanks under average operating conditions the roof is nearer to the gasoline surface than with tanks of more normal proportions.

In conclusion, there is no doubt in the author's mind that evaporation losses calculated by the above method are definitely conservative. Even so, their magnitude is surprising to many operators, and the savings that can be effected, by very simple means, both in product and hard cash, are not generally realized. It cannot be too strongly emphasized, however, that such savings can only be achieved by continuous attention to equipment. It is just a sheer waste of material, money, and effort to provide pressure tanks and efficient pressure–vacuum valves if roof manholes and/or dip-hatches are left open or not maintained in gas-tight condition. Foam connexions also need attention, to ensure that the gas-tight rupturing diaphragm is intact. It is felt that laxity in attention to such matters is in the main due to lack of appreciation of the magnitude of evaporation losses and consequently of the possible savings to be achieved by proper attention to tanks and equipment, and if this paper serves to stimulate the interest of those concerned, it will have served a useful purpose.

Finally, and quite apart from the main subject matter of this paper, Fig. 7 is included as a matter of general interest. It is the temperature record in the vapour space of a tank in Colombo, 80 ft diameter by 30 ft high. The weather was hot and sunny, as evidenced by the temperature range of nearly 40° F, but on the second day there was a downpour of rain at 4 p.m. Attention is drawn to the phenomenal rate of temperature drop, the curve practically following the vertical line ordinate over a range of almost 30° F. The rate of temperature drop is certainly not less than

30° in 15 min, and the consequent contraction of the air–vapour mixture in the vapour space of a tank of this size means an intake of air through the pressure–vacuum valves at the rate of over 34,000 cu. ft per hr. This caused a radical modification in our ideas as to the number and capacity of valves to be provided, which previously had been based primarily on pumping rates plus a safety margin.

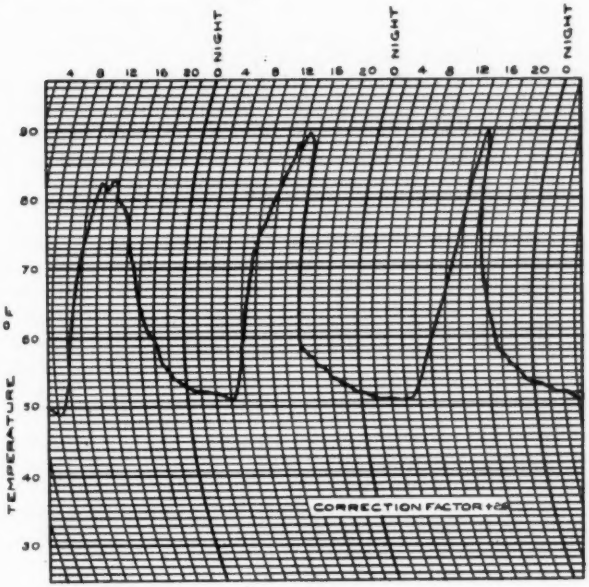

FIG. 7.

TEMPERATURE RECORD FROM TANK AT COLOMBO, 80 FT DIAM × 30 FT HIGH.

DISCUSSION.

THE CHAIRMAN : I think you will agree that Mr Sarjeant has given us a paper which has exercised our minds on this particular topic and will stimulate considerable discussion.

I propose to exercise the Chairman's privilege by not participating in the discussion.

I would make one comment, however. I think Mr Sarjeant dealt with a most important point when he stressed the significance of making clear to those who handle petroleum products, whether in the storage or distribution stage, the intrinsic value in terms of cash of those products which might be lost, either through bad handling or faulty or antiquated equipment. I think that applies not only to evaporation losses, but all through the marketing and distributing operations of the oil companies. To the field or refinery operator it is important to know what the operating losses

are in terms, say, of cubic feet of gas or percentage throughput. But, if when the value of the product is at its highest, on the marketing side, the staff is made to realize what is the equivalent in currency of the losses incurred, I am sure a much greater interest in this important question of loss control will be aroused.

MR G. C. CARR: It has been a very great pleasure to listen to this excellent paper, as conservation of gasoline is a long-standing headache for everyone connected with marketing operations.

I should like to put just one question. When the author asked what more we can do, he made no mention of heat-resisting paints, so I would invite his opinion as to the efficacy of aluminium paint, and particularly Titan white paint, which is in common use in the United States for reducing the transmission of solar heat through tank-roof plates.

MR R. E. ADLINGTON: I would like to offer my congratulations to Mr Sarjeant on his excellent paper. It appealed to me particularly because it is an engineering paper of a practical nature and is of interest not only to operators of marketing installations, but also to those concerned with refineries. Most of my own experience has been confined to refinery tankage, and I have had constantly to keep in my mind that Mr Sarjeant is talking of marketing installations, where, as you know, standards are not quite the same.

May I refer to the statement that throughout the world the conclusion is that the average temperature range in the vapour space of exposed above-ground tanks can be taken as 30° F. The author comments that that might cause some surprise. I must admit that it caused me a great deal of surprise, because those of us who have spent quite a lot of time in the Middle and Far East, as the author rightly suggests, find that the temperature range is very much greater than 30° F. Figures which I have looked up this afternoon confirm that in the Persian Gulf region, for instance, a temperature range of 50° F is by no means uncommon. The author has said that the data he quotes were obtained from the United Kingdom, Japan, Australia, Singapore, and Colombo. Since the average range is apparently so small, I assume that many more places in the world were considered when computing that average.

I was also very interested in the effect of pressure and vacuum valves, which in Mr Sarjeant's organization are set at + 8-in and − 2½-in water gauge. He indicates that the pressure and vacuum valve with that setting will not open or close over a range of 14° F which, based on the average temperature range he has quoted, represents a saving of evaporation losses of 14/30 or roughly 50 per cent. However, in cases such as I have mentioned where the temperature range is 50° F, it will be appreciated that the saving due to fitting pressure and vacuum valves is reduced from about 50 to 28 per cent. With a temperature range of 50° F, therefore, the significance of the pressure and vacuum valve at the settings stated is not so great as it would be over the range of 30° F.

Another small point is concerned with the insulation or lagging on the roofs. The author states that "under all-round average working condi-

tions it is found that the provision of lagging on the tank roofs reduces our residual losses by fully 50 per cent." In the case I have instanced, therefore, if we save roughly 30 per cent by fitting pressure and vacuum valves, should we save another 15 per cent by the addition of insulation, making 45 per cent saving in all? I do not quite see the logic of that, but there may be a very good reason.

Then with regard to the American practice of setting pressure and vacuum valves at + 1-in and − 1-in water gauge, which virtually relegates them to the status of mere draught excluders, he suggests it is for this reason that the so-called vapour conservation devices are employed. That may be right, but I suggest that in America they rather tend to use fixed-roof tanks only for the storage of black oils, and that they go to the more elaborate tanks for white-oil storage where evaporation losses can be so much greater.

I was most interested in the flotation method of dispensing which Mr Sarjeant has illustrated, for it must have great possibilities in connexion with light products; all except aviation spirit where water plus aviation spirit is anathema!

The author says it is assumed that the temperature of the liquid gasoline in the tank is constant, even at the surface, and that the temperature in the tank is unaffected by variations in temperature in the vapour space above it. I cannot quite see why that assumption is accepted, since I feel that there may be a considerable difference of temperature throughout the volume of oil with varying conditions of storage.

The author has mentioned that the pressure and vacuum valves and the roof insulation are very good means of reducing evaporation losses, and he has touched on other devices. It occurs to me that in marketing installations further consideration should be given to the development of semi-pressure storage, *i.e.*, storage of gasoline in tanks or hemispheroids at, say, 2½ p.s.i. In a hemispheroid, for example, it is said that aviation spirit can be stored for a period of two years without fear of its going off specification; but that is an expensive hobby. Can the author say what is the total cost "erected" of a hemispheroid *vis-à-vis* a conventional steel tank of equal capacity? Can he also indicate the operational and maintenance costs for a hemispheroid as compared with those of an ordinary tank? I have no reliable figures on those particular points.

Then there is the possibility of the full spheroid which can be operated at pressures of 10 p.s.i. and higher.

From technical literature issued by very worthy firms in America, one obtains an idea as to when this or that type of tank should be used. I wonder whether we should not revise our views on the whole subject of the suitability of tanks for various duties and try to create a code of usage for tanks? I know that each individual organization has thought about that very carefully and has its own ideas, but I suggest that it is a matter for standardization so that all companies could have the best possible advice as to the employment of particular tanks for particular purposes.

In conclusion, I would again thank the author for his paper and for giving us a great deal of food for thought. I, for one, will now get busy.

Dr H. G. Koefoed: I think we should all congratulate Mr Sarjeant on the very interesting paper he has given us, which I think is a very fine piece

of work. On the other hand, on certain points I do not agree with the points of view that he has put forward.

Reference is made to the percentage of gasoline vapour in the air–vapour mixture in the vapour space of the tank. The author states that all we need for determining the proportion of pure gasoline vapour in the vapour space of the tank under saturation conditions is the vapour pressure of the gasoline and its temperature. The assumption that it is under saturation conditions is one which should not necessarily be made. If we have a tank which is cooled down during the night, and which has the sun shining on it during the day, we get heating of this side. I have carried out some experiments in this connexion in which I have put a thermometer into the surface of the liquid, one in the middle and another at the top on the space above the surface (Fig. 1). Within a few hours there was a quite consider-

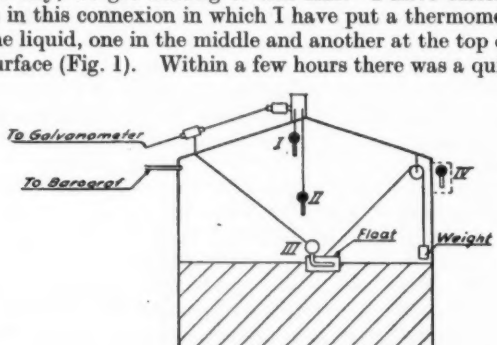

FIG. 1.

able temperature rise at the surface of the liquid, there was a considerable rise at the top of the tank and a certain amount in the middle of the space. We must not forget that when the temperature of the surface rises, the vapour pressure will rise. But the benzine will not evaporate, by reason of a cold layer of air just on top of the surface. There is no means of getting that air heated and therefore it will lie on the surface and seal the vapour.

The temperature in the middle of the space was 2·4° C when we started in the morning, and it remained very much the same all through. The temperature of the surface was 5·2° C at 7 a.m. and it was 10·8° C at 1.30 p.m. At the same time the amount of vapour was 25·4 per cent at the top of the space and 25·8 per cent at the bottom. The figure of 25·8 per cent is the saturation point of the air at 4·1° C, which is the temperature of the air–vapour sample at this point. That means that we have not to calculate for the extra vapour pressure arising from the temperature.

The question has been raised as to what more we can do to reduce evaporation losses. Marketing plants have this in common, that every day benzine is drawn from storage. We have devised a method for analysing the vapour content in the air, and we have found the point at which the air has the least concentration of vapour. We say that that is the point at which we want to allow the air to escape and we want to prevent it escaping from other places. We have connected all the air spaces in the different tanks—main tanks and filling tanks—with a 3-in gas line, thereby insuring that every gallon drawn from the installation

helps to prevent the breathing. If it can be ensured that the air escapes from a point at which the concentration of vapour is least, a lot of gasoline and money can be saved.

I would refer anybody who may be interested to my paper * and would say that I think it is impossible to construct a relief valve with a metal-to-metal seal or even with a flexible seal which will keep tight. In my experience a relief valve with liquid seal is far more reliable.

MR J. W. MARTIN : I should like to express congratulations to the author in so ably summarizing the work done largely at his instigation over a period of years. It is an achievement of major importance to save a high percentage of the possible evaporation loss in a widespread marketing organization by following consistently the principles enunciated perhaps twenty years ago.

Our Institute is also to be congratulated on the direction it has taken to provide an engineering paper of this quality. This is particularly so when it has taken the form of a practical exposition based on well-accepted basic principles. It is to be hoped that the occasion marks a fuller recognition of the importance of focusing attention to the distribution and storage activities of the petroleum industry. It should be remembered that every barrel of oil found and produced and refined has to be handled, transported, and marketed in the condition or to the specification required.

It is on this point that I would like to take up with the author the limit of the field he has surveyed and the considerations which have led him to so limit his survey. He had excluded losses in refinery processing or storage tanks because the product is a cheap and duty-free one. Would not the author agree that even duty-free losses are well worth while saving? Taking conditions in Great Britain, when it is remembered that the landed price of motor spirit to-day is approximately 9·5*d*. per Imperial gallon, can it not be assumed that the gasoline produced at present here, or to be produced by the new U.K. refinery building programme, will be worth roughly that amount? The value of the spirit itself is roughly equal to the present duty of 9*d*. per gallon. Obviously customs-paid savings are doubly worth while, but has not the picture changed on further evaporation prevention efforts since, say, 1938, when the landed price of spirit in the U.K. was approximately 4*d*. per gallon and the duty was the same as at present, namely 9*d*. per gallon? Presumably the same considerations apply elsewhere in a world marketing organization. For this reason, does not the author agree that there is a case for the re-evaluation of the problem of capital equipment at frequent intervals, or alternatively, on each occasion a new terminal or spirit-marketing installation is under consideration?

For the basis of capital equipment we can take an A.P.I. tank as the cheapest, the author's lagged pressure roof as representing a considerable extra expenditure, and we can advance progressively to storage tanks or vessels giving a higher range of operating pressures—or, to use the author's term, a larger permissible daily temperature variation. Progressing onwards in the types of equipment, there are the variable-volume vapour-

* Koefoed, H. G. " Gasoline loss control and molecular weight determinations," *J. Inst. Petrol.*, 1946, **32**, 529–574.

space types, and finally the floating roof. Whilst the increase in cost of these various types of equipment since before the war must be recognized, the relation between capital outlay and increased price of motor spirit does seem to justify further scrutiny of the problem, and I hope the author agrees.

May it not be worth while going after the 25 per cent remaining after the author has in round terms conserved 75 per cent of the possible loss. Therefore, I feel that differentials in the price of the various types of equipment that have been mentioned are ones which need scrutiny, not only at frequent intervals, but in relation to the value of the product in various parts of the world with a view to seeing for high-spirit-price areas whether higher capital outlay would not bring a better return by saving some of the remaining 25 per cent—using the author's figures for the relative losses.

No doubt others will raise some points of perhaps more pertinent nature. I cannot resist, however, pointing out that freely vented conditions giving rise to the 200 g.p.d. loss are not allowed to occur even in the land of plenty. The inherent design of a pressure-roof tank with its relatively steep slope unfortunately presents the large vapour space mentioned by the author, whereas the A.P.I. roof of equivalent size with its flatter slope of 1 in 12 gives not 280,000 cu. ft. but nearly 10 per cent less for the size of tank considered. This means a reduction of 28,000 cu. ft. in the daily " breathe", and hence a loss lower than the 200 g.p.d. mentioned, namely 181 g.p.d. Having suggested that the losses with the American type of roof need not necessarily be so great as the author implies, it can be pointed out that the relatively cheap U.S. domestic price of motor spirit has not hampered the development of special devices, although the author has suggested that losses where motor spirit is cheap are less urgent.

It has not occurred to me that the film of wet gasoline left by the descent of a floating roof was a serious contribution to the admittedly small loss which occurs with this type of tank. I wonder if the author could adduce some facts to back his statement. With the increased tanker discharge rates it can quite well be imagined that a 10,000-cu.m. floating-roof tank will be filled in less than 10 hr. This process will not, of course, cause the loss (film) referred to by the author. It is rather in the reverse direction when this might occur, but would not the author say that such discharge rates and consequent downward movement of the floating roof are unusual in a marketing tank? I am inclined to suggest that where loss does occur with a well-designed floating roof, it is due to windage and either the effect of scooping or shell flexing which would be more apparent on the older type of riveted tank and sealing shoes which have of necessity a relatively small radius of curvature. I think it can be accepted that it has been shown with a butt-welded tank and the deeper type of continuous-sealing shoe that the loss is reduced to a very low figure whether it is caused by wind, or otherwise.

May I add a plea to reinforce the author's point about dip hatches, foam connexions, and other fittings being repeatedly checked? It is, in fact, a plea that the high standards of efficiency in the control of refining operations may be adopted in the operation of storage plant. A liquid leak in the shell of a tank would not be tolerated. Something would be done about it, but all too often vapour escapes equivalent to a spirit leak of considerable

magnitude and this passes unrecognized. Whether this is due to faulty roof fittings, or relaxation of effort on storage-tank control, such vapour leaks are preventable and must not be allowed to pass unnoticed. They never should be accepted as inevitable.

I hope these remarks are considered appropriate to what I believe is the first public statement here of fundamental rules governing the engineering procedure of a marketing company whose evaporation-loss figures must obviously be small. We have been given an authoritative statement, and I expect, not for the first time, to learn much from the author's reply to the discussion.

Mr W. A. Russell: I should like to ask whether Mr Sarjeant could give us some idea of the type of lagging he has used on his tanks and the sort of thicknesses he uses.

Mr R. F. Bishop: The author has given a most valuable account of evaporation losses and some most interesting results of tests. In his account of the methods of reducing losses he has surveyed very fully the reasons which led to the adoption of the lagged 8-in water-pressure and 2½-in vacuum tank, but has touched very lightly on some of the other possibilities.

One of the most fruitful of these is the use of tanks capable of withstanding a larger range of pressure. The range required to prevent all losses may easily be calculated from the data given in the paper. If a 10½-in water-gauge range prevents all losses due to a 14° F temperature range then a 30° F range would require a 22½-in range of pressure for complete loss prevention (this could best be achieved in practice by a 20-in pressure and a 2½-in vacuum).

In order to see whether such a tank could be used economically we may compare it with the lagged 8-in type. With this tank the loss of 50 g.p.d. estimated by the author at 9*d*. per gal would amount to a loss of £700 per year. Taking a five-year period for paying off capital this gives a maximum extra cost of £3500. The higher pressure tank would require no lagging, and since this costs several thousand pounds it suggests that the extra cost of the tank might be as high as £5000 and still show a considerable net saving. The figure is surely large enough to suggest that the author's remark that " the remaining margin of loss is so small that the capital cost of such devices cannot be justified by the potential saving " may not be a fair one.

The author draws attention to the need for maintaining pressure tanks in a pressure-tight condition, and to do this effectively measurement of the tank contents must be carried out under pressure-tight conditions. Although the author does not refer to it in the paper I know that he has given this question a great deal of attention. The present dipping methods give a high degree of accuracy, but for pressure tanks it might well be worth considering the use of float gauges with an outside indication of the tank liquid level. Whatever method is employed for the effective operation of such tanks, much wider use will have to be made of pressure dipping or other such methods.

The next point to which I would like to refer is the assumption of 100 per

cent saturation of the gasoline-vapour–air mixture expelled from the tank. Some very useful figures are given in a paper by M. H. H. Radier entitled "Reduction des pertes par evaporation d'hydrocarbures legers stockes en reservoirs a toits coniques fixes."

In this paper he describes a test in which an empty tank was half filled with gasoline, and the proportion of vapour measured in the air–vapour mixture expelled each day. The proportion of vapour in the mixture increased almost uniformly for seventeen days, when it reached a constant value corresponding to 90 per cent saturation. M. Radier considered that the figure of 90 per cent only was caused by dilution with fresh air breathed in each night.

MR W. E. FRANKENBERG: I should like to make a remark about the degree of saturation. Some years ago we carried out some experiments on the concentration of gasoline vapour in the spaces in the tanks, with a view to determining the safety or explosive limit. After filling the tank we found that for a few hours the vapour space about 3 ft above the surface of the liquid was saturated, and at 12 ft it had less than half the saturation value of the benzine vapour. Equilibrium was established in roughly four days.

When emptying the tank the same conditions were observed, but equilibrium was usually established within about 24 hr.

After pumping spirit into the tank which had been gas-free, I think it took something like seven days to establish equilibrium in the vapour space.

MR H. PHILLIPS: I should like to thank Mr Sarjeant for his very practical and interesting paper. We see that the pressure-roof tanks take care of approximately 50 per cent of the losses and the lagging takes care of another 25 per cent. What can we do with the remaining 25 per cent? I think the saturation point comes into the picture here. If you wanted to jet mix your gases you would put your jet just where we have our pressure and vacuum valves. During the evening, when the vacuum is 2½-in, the air is coming in at a fair velocity and must cause a tremendous amount of turbulence in the vapour space which would no doubt go down to 10 or 12 ft and cause a quick saturation of the vapour space. Could we put in baffles to prevent that jet mixing taking place? The air would then come in and would be guided by the baffles across the top of the tank. It may be that in looking after the vapour space we have scope for economy.

MR PETER KERR: We are all grateful to Mr Sarjeant for his paper and for re-opening discussion on so important a subject.

In connexion with the Chenicek–Whitman method, would Mr Sarjeant say how many samples per tank are usually found to be sufficient, and also whether different average loss figures have been found at different verticals in the same tank. The evaporated spirit may, of course, not distribute itself uniformly across the tank.

At what levels in the vapour space were the temperature recorders operated, and is there a calculable level at which one obtains the average temperature of the vapour space?

Mr Sarjeant makes the important suggestion that it is desirable to in-

vestigate whether air that is drawn into a tank overnight is completely saturated with oil vapours before it is breathed out next day. I have seen figures which suggest that diffusion of gasoline vapour throughout the air space in a tank is quite slow. I agree with Mr Phillips that the effect of baffles under the relief valves might be tried. Reference was made by Dr Koefoed to the blanket of gas which lies just above the oil surface, and conservation of that blanket is one of the points which would be aimed at in providing baffles under the relief valves.

Mr W. L. Coats: Mr Sarjeant has worked out the extent of the losses, assuming 100 per cent saturation in the vapour space, and some speakers have discussed whether or not there would be 100 per cent saturation. It would appear that the answer to this could be obtained very simply by comparing the actual losses with the calculated losses. Can Mr Sarjeant give us information on that point?

Another point is, what would be the effect of high concentration of water vapour in the air? Would it be sufficient to limit appreciably the amount of spirit which could be absorbed in the air space?

With regard to the lagging of the tank, how does this affect maintenance? Is there any evidence of corrosion, rusting, etc., taking place under the lagging? If so, does it mean stripping off the lagging, and how often, in order to give proper maintenance to the tank shell?

For the purpose of dipping pressure-roof tanks special equipment is obviously necessary and has been designed. This, I understand, functions fairly well within limits, but is cumbersome and awkward.

Is there any equipment available which enables dipping to be done with reasonable facility, especially at frequent intervals as when keeping a check on a tank which is being filled at a high rate of pumping and the liquid is approaching the upper limit.

Mr F. W. Rischmiller: Mr Sarjeant's paper has dealt primarily with pressure-tight roofs. There are still some hundreds and probably thousands of low-pressure roofs in existence, and in tropical climates.

We have found that the use of roof lagging, high water bottoms and water spray have served a very good purpose in having brought our losses down to figures very closely approaching the losses from a high-pressure tank. I wonder whether Mr Sarjeant has any experience which would bear out our results? We all know there is very great difficulty in checking losses; I think Mr Sarjeant appreciates that.

Secondly, there is the question of type of vacuum and pressure-relief valve to be used. He has mentioned the mercury-seated valve. There are also metal-to-metal valves. Can he give his opinion on the relative merits of the two?

Thirdly, the paper is entitled "Evaporation losses at marketing installations," but it deals primarily with the evaporation losses by breathing. I would suggest that the losses by breathing are not the major losses in a marketing installation; in point of fact they are about one-third of the total losses. The remaining two-thirds are also mainly due to evaporation, and I would like to ask for Mr Sarjeant's views on methods he would recommend to reduce the two-thirds.

MR SARJEANT: When I came here this afternoon to address the meeting I was impressed by the galaxy of talent before me, and I felt that some apology was due from me for having put the paper in such simple form, cutting the frills, and making it perhaps more elementary than is warranted, but I put it forward in order to promote discussion and interest, and from the number of questions that have been put, I feel that it has at least done that.

In reply to Mr Carr's question concerning the relative values of different paints on the tank roof, we actually carried out experiments by suspending recording instruments in the roofs of tanks of identical size and shape, side by side, in one case painted aluminium and in the other case painted Titan white. The experiments covered a period of six or eight weeks so that we obtained fairly good average results. The Titan white paint showed up better from the temperature-range point of view; on the average there was about 6° F less temperature range under the Titan white painted roof than under the aluminium painted roof. The maximum difference we ever found was about 10° F. On the other hand the Titan white paint is not so durable, not so weather resisting, and so on, as aluminium paint. We were aware of the temperature advantages of Titan white paints before we decided to go in whole-heartedly for aluminium. On economic grounds we felt justified in adopting aluminium, because the reduced evaporation losses when using Titan white would be more than compensated for by the increased cost of maintenance of the tank roofs.

I was very interested to hear the figures quoted by Mr Adlington representing conditions in the Persian Gulf. I mentioned in the paper that I had not the least doubt that, in parts of the Middle East, the temperature ranges would be much more than 30° F, and it is good to have that supposition substantiated by one who knows that part of the world so well. A temperature range of 50° F does not seem out of the way for that area, and, of course, a range of 50° F will increase the losses from the tank of the size I mentioned in the paper from about 210 to 350 g.p.d.; the loss will be directly proportional to the temperature range. So that, although the fact of putting pressure and vacuum valves on a tank of that nature tends to save only 28 per cent of the potential loss, as against 50 per cent in the average pressure tank working under a 30° range, that 28 per cent represents a very substantial amount and is just as much as 50 per cent of 210 gal. In other words, the saving due to pressure and vacuum valves will be of the same order. Mr Adlington will probably agree with that.

I agree with him entirely that the effect of lagging is independent of the setting of the pressure and vacuum valves. If you put lagging on a lower-pressure tank you would get just as much benefit from that lagging as if you put it on a tank of higher pressure. It is just a matter of coincidence that in our particular tanks the lagging saves 50 per cent of our residual losses.

It was suggested by Mr Adlington that in the United States the use of fixed-roof tanks is confined to black oils only. I am not very familiar with conditions in the States, but apart from what I have read, I think his statement is rather sweeping. I do know that in the early 1930's the Standard Oil Company carried out a test which extended right across the Continent

of North America. They had more than 100 tanks segregated over a period of twelve months; they were cylindrical, cone-roofed, tanks used for storing gasoline, and they ascertained the average evaporation losses from those tanks over that period. It is a matter of interest that the figure they arrived at in respect of those 100 tanks during twelve months was 6·5 U.S.G. per sq. ft. of surface per annum; that is equivalent to 5·4 I.G. If you take the same American tanks and deal with them on the basis I have suggested over a temperature range of 30° F, averaging all sizes of tanks from 120 to 30 ft diameter, you will find that the resulting loss works out at about 4·84 gal per sq. ft. of surface per annum. But I suggest that 30° is not a sufficient range for American conditions, and that it will be slightly higher; the range in the U.K. is 30° on the average. If the range is 33° instead of 30°, it will increase the 4·84 gal to 5·3 gal, which is in very close agreement with the actual figure of 5·4 gal. The method of calculation is probably conservative, but the results are reasonably close.

Then Mr Adlington feels that there is a definite temperature rise at the surface of the gasoline. That is a point which I have argued with many people, and I am quite prepared to agree, as I think I suggested in my paper, that if the gasoline level is high in the tank, and if there is direct radiation from the roof, you will undoubtedly have quite an appreciable rise of temperature at the surface of the gasoline. But under normal operating conditions and with a reasonable margin between the roof and the surface of the spirit, I have not been able to find a case which does not indicate that the temperature rise is of negligible importance.

Reference was made to the use of higher-pressure tanks—hemispheroids and the like—to eliminate losses. I agree that if you build a vessel strong enough to withstand sufficient pressure, you will completely eliminate the breathing, at a price. It is purely a matter of economics. If our tank constructors, who are well represented here this afternoon, can give us a higher-pressure tank at reasonable price, so that the additional cost of the higher-pressure tank is paid for by the saving of the 50 g.p.d. that we are now losing from our largest tanks, we are quite prepared to consider it. In fact, we are seriously considering the adoption of higher pressures for our normal operation. We have not very much margin to play with, but if the elimination of losses justifies the increased cost of the higher-pressure tank we are prepared to consider the use of higher pressures.

We have thought so much about gasoline vapour, air–vapour mixtures, and so on that Dr Koefoed's contribution has come like a breath of fresh air from Denmark. Dr Koefoed's views were very much appreciated, and I was particularly interested by his suggestion to take off the vent at the point of leanest mixture. I agree entirely that that is a very important matter, well worth looking into and I propose to look into it.

Then he referred to the fact that there is a rise of temperature at the surface of the spirit due to heating through the tank shell, and on the other hand there is no rise of the vapour concentration. Of course no rise of vapour concentration means no rise of pressure.

I am very glad that support has been given to the liquid-seal type of valve, and the view has been expressed that it is impossible to make a vapour-tight valve of metal-to-metal construction or even with a flexible seating for such low operating pressures.

In reply to Mr Martin—he has taken me to task somewhat for suggesting that evaporation losses are important only in the case of marketing installations, and has asked why refineries should not be included. I think he knows me better than that. I think evaporation losses at refineries should be given as much attention as those at marketing installations. I think the opening remarks of the paper make it clear that when I suggested losses at refineries were less important, I was speaking from the point of view that gasoline would be in stock for shorter periods at the refineries than at marketing installations, and therefore the losses would be less important in magnitude over the year; whereas in marketing installations, where we have long-term storage, the losses are occurring all the time. The annual loss is a function of the length of time the spirit is in the tank, which would be less at the refinery than at the marketing installation.

I agree entirely with Mr Martin that it is worth while going after the remaining 25 per cent of losses; if we can save that 25 per cent, well and good. Give us the tools and we will finish the job!

Apropos his comments on vapour leaks; that is tied up with the question of dipping, which is in itself a cause of major vapour leak. It is easy to demonstrate that if you dip one of these large tanks which is operating under 8-in water-gauge pressure—one of the 118 footers—you naturally lose pressure by dipping through an open hatch. The actual loss of liquid gasoline in a temperate climate amounts to approximately 50 gal in one dip, and in the tropics it is something like 70 gal. I have pointed out to the dippers that if they saw their chum walking around the property and emptying a 50-gal drum down the drain, they would say something about it; but simply because the gasoline is lost as vapour from the top of a tank, they thought nothing about it.

A question was asked by Mr Russell concerning the type of lagging we used. We have concentrated almost entirely on cork; we buy the cork in slabs 2 in thick with dimensions of 3 ft × 1 ft, and they are set in bitumen on the tank roof. The whole roof is covered with bitumen and the cork is set in it, grouted with bitumen at the joints between slabs; the cork is then given a covering of bitumen, and on top of that we apply two layers of weather-proof canvas, which is painted with aluminium paint. Provided the work is properly done, and that the weather proofing, in particular, is given proper attention, we experience no corrosion underneath the lagging. If you permit a flaw in the cover, or if the cover is damaged so that water saturates the cork, then corrosion is liable to occur underneath.

Mr Bishop gave some interesting figures and pointed out that $22\frac{1}{2}$-in pressure range would cover our 30° F temperature range. I agree entirely. He suggested that the vapour in the vapour space is 90 per cent finally, whereas Mr Frankenburg said it was saturated at 3 ft above the surface and only 50 per cent saturated at 12 ft above the surface. There is evidently a wide diversity of opinion as to the degree of saturation in the vapour space. If you technologists cannot agree on the subject, we poor engineers cannot hope to do so!

I agree entirely with Mr Phillips that the inrush of air is important. Unfortunately we have not figures to prove it, but in the old days we mounted our pressure and vacuum valves around the periphery of the tank roof close to the top of the shell so that the inrush of air would cause

tremendous agitation of the vapour adjacent to the surface of the liquid gasoline, and would give rapidly a high concentration. We now put the valves as near as possible to the apex of the roof as far as possible from the surface; in some cases we have actually provided baffles underneath the valves to divert the air stream. I am sorry we have no figures to show whether or not that has produced any startling results.

A certain amount of doubt was expressed by Mr Peter Kerr about the Chenicek–Whitman method. Quite frankly, were I not a poor engineer standing before oil technologists, I myself would have expressed some doubt about it, but I thought it was so well recognized and accepted by technologists that I dared not say anything against it! There is, of course, the difficulty of sampling, which can be overcome by exercising great care; but I feel there is another possibility of error—about which I may be quite wrong—that with the apparatus you take every precaution to ensure that the whole volume of the spirit sample under test is submitted to the successive stages of evaporation. In the case of a storage tank, the temperature is, in the main, applied at the top surface of the spirit. The lighter fractions are driven off, resulting in an *increase* in specific gravity of the surface layer, but this is offset to some degree by the temperature rise at the surface which tends to *reduce* the specific gravity. I ask you technologists which wins? It is suggested that due to these opposing factors circulation is likely to be sluggish and may result in a deeper " cut " being taken from the surface layer, giving a result which is not strictly comparable with the results of Chenicek–Whitman tests carried out under laboratory conditions.

With regard to the levels at which we took temperatures, before we started we wondered which were the best positions for the recording thermometers. We had two recording thermometers, and for the first week one was placed in the centre of the vapour space and one was placed under the apex of the roof. During the next week we had one in the centre and one just above the spirit.

During the third week we had one in the centre and the other adjacent to the tank shell on the sunny side, and so on. We explored the whole of the vapour space, and, as we expected, the instrument suspended in the centre of the vapour space gave as nearly as possible the average conditions in that space. It was just as well to prove it.

A question was asked by Mr Coats about the actual losses as compared with the calculated losses. I have already referred to the American trials over 100 tanks in which the actual figures were compared with the calculated. We have some actual figures from these Chenicek–Whitman tests. In the 91-ft diameter low-pressure tanks (3-in pressure), the actual loss was 1·44 gal per sq. ft. per annum, whereas the calculated loss was 1·36—rather too close to be true! In the case of the 98-ft diameter tank (very shallow, only three courses high) having an unlagged top, the Chenicek–Whitman loss was 3·87, whereas the calculated loss was 2·4 gal per sq. ft. per annum. That rather substantiates the suggestion that in these shallow tanks, we get additional heating of the surface layer by radiation from the roofs, resulting in an increase of vapour pressure and consequently of vapour concentration, and therefore we may expect the loss to be that much higher. In the case of an unlagged low-pressure tank, strangely enough the Chenicek–

Whitman and the calculated figures were identical at 4·62 gal per sq. ft. per annum.

Those figures, taken at random, indicate that we have a reasonable working basis. I do not claim scientific accuracy for the figures, but we know we can obtain figures of the right order and magnitude at all events.

Several people have referred to dipping. I agree that this dipping question is a serious one. There are various devices on the market for dipping tanks under pressure, but in general they are so cumbersome in operation that operators forget about them! If you don't keep an eye on the operators they will throw those devices to one side and dip through an open hatch. Frankly, I cannot altogether blame them. If it is simply a case of dipping to ascertain the level of the spirit in the tank, one can do quite a lot with floats and apparatus of that sort which will give a reasonable degree of accuracy. But when, in addition to ascertaining the spirit level, you have to take temperatures and so on, and in some cases samples of products, the devices are cumbersome to use.

Reference was made by Mr Rischmiller to losses from low-pressure tank roofs, and I agree that lagging and the use of high water bottoms, etc., will do quite a bit to reduce the losses. The tanks at Hong Kong were low-pressure tanks, and there, by means of high water bottoms, we achieved just as low losses as with high-pressure tanks and lagging. Water is not always available, however. Water spray brings its own problems, and unless it is intelligently applied, you can still have quite big losses. You can cut off the water supply, but you have evaporative cooling which persists for an indeterminate period after cutting off the water supply. Nevertheless, the spray has worked successfully when used with great care.

Then Mr. Rischmiller spoke about the comparison of types of pressure and vacuum valves. We have decided that the liquid-seal type is the only one that is gas-tight, and a pressure and vacuum valve that is not gas-tight is not to be recommended; it can completely nullify the advantage of the pressure-roof tank.

Finally he spoke of the total losses in installations. My paper was deliberately entitled "*Evaporation* losses at marketing installations"; if you are expelling vapour mechanically, *e.g.*, by filling a tank with spirit, it is as well that it should be kept out of the discussion for the moment.

Vote of Thanks.

The Chairman: You will wish me to express to Mr Sarjeant our very warm thanks, not only for the paper he has presented to us, but for the further enlightenment he has given us in the handling of the discussion. He went to an abnormal amount of trouble in dealing with all the questions raised, and I think he has satisfied every enquirer who wanted further information. The able manner in which he handled the whole thing is very gratifying to all of us, and we wish to extend to him our best thanks.

As a Member of the Council, I am convinced that meetings of this nature, where subjects are dealt with in the manner in which Mr Sarjeant has handled this one, where questions and experienced views are put forward by members and visitors in the discussions and further information is

elicited from the author—such meetings are features of the Institute's work by which we can very well say we are serving the industry well.

We have been particularly fortunate to-day in the amount of information Mr Sarjeant has conveyed to us in his paper, and subsequently, and I feel sure you will wish to express to Mr Sarjeant warmest thanks on your behalf and that of the Institute, for his work.

(The Vote of thanks was heartily accorded and Mr Sarjeant briefly responded.)

CORRESPONDENCE.

"Emulsions of Sea Water in Admiralty Fuel Oil with Special Reference to their Demulsification."

To the Editor, *Journal of the Institute of Petroleum.*

SIR,

Mr Mumford's letter on page 140 contains two complaints: (*a*) that we have regarded Admiralty fuel oils as though they were "representative of all boiler fuels" (I presume that he means boiler fuel oils, since I understand that coal is still used for firing boilers); and (*b*) that the description of emulsification as taking place "readily" and of the stability of the emulsions as "great" is "very misleading".

Since the title of the I.P. paper specifically restricts its subject matter to Admiralty fuel oils, complaint (*a*) seems to indicate only that Mr Mumford under-estimates the intelligence of readers. His excuse for writing his letter is that other journals may quote the paper; does he suggest seriously that they will do so without mentioning the title? As regards (*b*) the suggestion that the words complained of are used "in the absence of some indication of the conditions involved" is untrue; readers can confirm this for themselves. That the emulsions were not breakable by heating alone would seem to justify the use of the epithet "great" to describe their stability in accordance with the usual practice.

The penultimate paragraph says: "We have no reason to believe that commercial fuel oils emulsify as readily . . ." How does he make this comparison if, as he suggests, the word "readily" is so ill-defined as to "give a wrong impression"? I am surprised, Sir, to read in your Journal (page 140) a letter, criticizing a serious scientific paper, in which the only evidence justifying it begins with the words: "We have no reason to believe . . ." Has or has not Mr Mumford information of the emulsifying propensities of his fuel oils? His difficulty in finding samples of "sludge" is a *non sequitor*. Formation of sludge requires, first, contamination by a large amount of water and the sedimentation of the emulsified water to form the close-packed emulsion which is sludge. This process, as pointed out in the paper, proceeds very slowly. His failure to find it may be only a tribute to the efficiency of the Shell organization in avoiding water contamination, or it may be that he looked in tanks in which the oil had not stood for a time long enough for the sedimentation of the sludge.

While claiming that the paper makes it clear to readers that the experimental work and conclusions drawn from it are restricted to Admiralty fuel oils, I would say that the work also leads to the conclusion that all fuel oils are subject to this trouble and, further, that the stability of the heaviest oils is likely to be the greatest. I would add, however, that there is, I think, a maximum viscosity above which ease of emulsification of water decreases. No comparison is therefore complete unless temperatures are specified.

Since one reader seems to have missed so much in the paper, I should repeat that this problem was more serious in H.M. ships than elsewhere because seawater is deliberately brought into contact with the oil as part of operational procedure. Full credit should be given to the Admiralty for having sponsored this research. I may add that one of the greatest difficulties encountered in this work was the persistent refusal of users to admit the presence of water in their oil.

Yours truly,
A. S. C. LAWRENCE.

The University,
Sheffield 10.
February 2, 1949.